THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

DECEMBER 1927.

CIX. *Thermodynamic Integrating Factors.*

By Prof. A. PRESS *.

Introduction.

IT is rather generally believed that in any thermodynamic formula, or reasoning, it is sufficient to apply the universal integrating factor

$$\mu = \frac{1}{\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in order to obtain a condition that must hold unquestionably. It is the object of the present paper to show in what respects the integrating factor (1) needs to be taken, and, secondly, to show that the universality of application of such integrating factor is far from justified. In fact, for every μ there corresponds a particular thermodyamic path function.

In this connexion it may be recalled that the writer made use of an integrating factor with two variables to prove the Grüneisen-Ratnowsky formulæ for specific heats, and, when corrected, also the elasticity coefficients would naturally follow without having to make use of the Quantum Theory. In fact, Trouton's formula when generalized is also obtainable in this way.

The Integrating Factor and its Consequent Equation of State.

It has already been shown by the writer (see Phil. Mag. p. 431, Aug. 1926) that mathematically the condition for an

* Communicated by the Author.

integrating factor following from the fundamental equation

$$dQ=dU+pdv=dU+dW \quad . \quad . \quad . \quad . \quad (2)$$

is the equation :—

$$p+\frac{\partial U}{\partial v}+\frac{\frac{\mu}{\partial\mu}}{\frac{\partial}{\partial\theta}}\cdot\frac{\partial p}{\partial\theta}=\frac{\frac{\partial\mu}{\partial v}}{\frac{\partial\mu}{\partial\theta}}\cdot\frac{\partial U}{\partial\theta}. \quad . \quad . \quad . \quad (3)$$

Naturally, if we assume an integrating factor of the form (1), then on the simplifying assumption that we make

$$\frac{\partial U}{\partial v}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

it results that

$$p-\theta\frac{\partial p}{\partial\theta}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

No other Equation of State can possibly follow from (5) than that (on integration)

$$\left.\begin{array}{l}\lg p=\lg\theta-\lg\left\{\frac{a}{1}f(v)\right\}\\ p\,.\,f(v)=a\theta\end{array}\right\}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For the so-called "perfect gas," writing for simplicity

$$f(v)=v \quad \text{and} \quad a=\mathrm{R}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

we naturally have the "Equation of State"

$$pv=\mathrm{R}\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Yet the question may well be asked, how to obtain from (3) the characteristic equation for the adiabatic expansion of a "perfect gas" if μ is to be assumed as a possible universal integrating factor? Surely this question is an all-important one for Thermodynamic Science.

Without attempting to introduce the necessary integrating factor in (3) at this time, it will first be desirable to obtain the characteristic for adiabatic expansion without making use of the relation (1), or the assumption of a perfect gas.

The γ-Ratio and Adiabatic Expansion.

By the first law of thermodynamics we have

$$dQ=dU+p\,dv. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Quite generally, however, must we also have that

$$d(pv)=p\,dv+v\,dp. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Introducing the latter in (2) gives the equation

$$dQ = d(U+pv) + v\,dp. \quad . \quad . \quad . \quad . \quad (10)$$

The definition of adiabatic expansion is really determined by the relations

$$dQ = 0 = dU + p\,dv = d(U+pv) - v\,dp. \quad . \quad . \quad (11)$$

That is, by division in (11) we have

$$\frac{d(U+pv)}{dU} = -\frac{v}{p}\cdot\frac{dp}{dv} = 1 - \frac{d(pv)}{dU} = \gamma. \quad . \quad . \quad (12)$$

If then it should be found substantially that we can take

$$\frac{d(pv)}{dU} = \text{constant}, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

though *not necessarily the same constant for all gases for example*, it will mean in (12) that

$$\gamma = \text{constant}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Thus on integration we have that

$$\left.\begin{aligned} pv^{\gamma} &= \text{constant} \\ pv &= (1-\gamma)U \end{aligned}\right\}. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Of course, it is well known that the total heat of a body

$$I = U + pv \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

is not linearly related to the internal energy U, for we should then have

$$\frac{dI}{dU} = 1 + \frac{d(pv)}{dU}. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Ordinarily, anomalies occur. Thus (see Birtwisle, 'Thermodynamics,' p. 76), it was shown by Thomson and Joule in 1862 that the heat developed on compression may actually be more, or even less, than the corresponding amount of mechanical work on the compressing piston, depending on whether the substance was air, carbonic acid gas, or even hydrogen.

The Integrating Factor for Adiabatic Expansion.

To ease the mathematical work let us take then, as the fundamental conditions given, that

$$pv^{\gamma} = A\,; \quad \frac{\partial U}{\partial v} = 0^{*}; \quad pv = (1-\gamma)U. \quad . \quad . \quad (18)$$

* This virtually implies that the potential due to molecular forces or aggregations does not occur.

It is required to determine the integrating factor μ that shall satisfy (3) even when the path taken by the substance involves the element of adiabatic expansion or compression.

Introducing (18) into (3) we have first to take note that we can obtain $\left(\frac{\partial p}{\partial \theta}\right)_v$ from (18) for it necessarily follows that

$$v\left(\frac{\partial p}{\partial \theta}\right)_v = (1-\gamma)\left(\frac{\partial U}{\partial \theta}\right)_v, \quad . \quad . \quad . \quad (19)$$

provided, and only provided, no anomalies occur as mentioned above with respect to (13). The equation (3) then reduces to

$$\frac{\partial \mu}{\partial \theta}\cdot\frac{A}{v^\gamma} + \frac{\mu(1-\gamma)}{v}\left(\frac{\partial U}{\partial \theta}\right)_v = \frac{\partial \mu}{\partial v}\left(\frac{\partial U}{\partial \theta}\right)_v. \quad . \quad . \quad (20)$$

To integrate the latter equation we can provisionally assume that

$$\left.\begin{array}{c}\mu = VT \\ \text{with } V = F(v) \text{ only and } T = \phi(\theta) \text{ only}\end{array}\right\}. \quad . \quad (21)$$

Introducing (21) into (20) gives, after reduction and rearrangement of terms that we need to satisfy the relation,

$$\frac{1}{T}\cdot\frac{dT}{d\theta} = \left(\frac{1}{A}\cdot\frac{\partial U}{\partial \theta}\right)\left\{\frac{1}{V}\cdot\frac{dV}{dv} + \frac{(\gamma-1)}{v}\right\}v^\gamma. \quad . \quad (22)$$

For convenience we can write

$$\frac{1}{A}\frac{\partial U}{\partial \theta} = C \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and *assume* that

$$\frac{\partial U}{\partial \theta} = \text{constant}. \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Since the variables are separated we can equate each side to a constant α such that it follows

$$\frac{1}{T}\cdot\frac{dT}{d\theta} = \alpha\,; \quad T = \epsilon^{\alpha\theta}, \quad . \quad . \quad . \quad . \quad . \quad (25)$$

$$\frac{1}{V}\cdot\frac{dV}{dv} + \frac{(\gamma-1)}{v} = \frac{\alpha}{Cv^\gamma} = \frac{\beta}{v^\gamma}. \quad . \quad . \quad (26)$$

Solving (26) by bringing the v-terms to the right-hand side it is seen that we need to have V of the form

$$V = v^{1-\gamma}\cdot\epsilon^{\frac{\beta}{1-\gamma}\cdot v^{1-\gamma}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

* This is virtually the Grüneisen condition for solids, where v is substantially constant and $\frac{\partial p}{\partial \theta}$ connects with the elasticity coefficients.

In other words, the integrating factor *must* under the circumstances mentioned be given by

$$\mu = \mu_0 \frac{\epsilon^{\frac{\beta}{1-\gamma}} v^{1-\gamma}}{v^{1-\gamma}} \cdot \epsilon^{\alpha\theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Indeed, it necessarily follows that to each particular path thermodynamically pursued by a substance there corresponds a distinguishing thermodynamic integrating factor and not necessarily satisfying the relation $\mu = \frac{1}{\theta}$.

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Washington, D.C., U.S.A.,
June 1st, 1927.

CX. *Consequences of a Matrix Mechanics and a Radiating Harmonic Oscillator without the Quantum Postulate.* *By* Prof. A. Press *.

Summary.

In order to avoid postulating quantum conditions from the start, as done in the Heisenberg–Born–Jordan–Dirac Matrix Mechanics, the writer conceived the idea of giving concrete visualization to the elements of the pq–qp matrix by relating them to a classical formula leading to an action (see paper published in the Phil. Mag. for Sept. 1924). This required a slightly modified way of defining the unit matrix.

If we consider a portion of a radiating gas capable of sending out a series of wave-lengths according to an observed law, then we may attribute to each periodicity a sine element and an associated cosine element of the p and q matrices. Such aggregates, when expressed in the form of an action matrix pq–qp, constitute a standard diagonal matrix. In the text it has been shown that there is an analogy also between $h/2\pi i$ of matrix mechanics and the χ-expression developed on the basis of the present matrix system.

An important distinction has also manifested itself. On account of the special character assigned to the p and q elements in the modified matrices employed, the squares of the $p(mn)$ elements rather than of the $q(mn)$ elements are associated with the frequencies $\nu(mn)$. It must also be said that the χ-function does not require the i-term to appear in the denominator. Nor is it necessary, for matrix processes, to assume that the value of all the diagonal elements in the unit matrix shall be unity or even equal to each other.

* Communicated by Prof. A. S. Eve, F.R.S.

The requirement of the i-factor in the numerator has naturally led to the minus sign appearing when doubly differentiating a matrix, as occurs when considering the problem of an harmonic oscillator. Nevertheless, it must be borne in mind that the harmonic oscillator functions, heretofore used, have not been strictly radiating systems *. This is especially true since the Hamiltonian H-function has been considered as constant and independent of the time. The radiating harmonic oscillator of the text, on the other hand, implies that only the mean H over the cyclic period is constant. Thus, during a quarter of a cycle absorption of energy is allowed for, and mathematically expressed, whereas during the next quarter of a cycle, radiation of energy is presumed to take place. Besides, for a radiating oscillator, the momentum is not wholly in phase with $\dot{q}$. Thus the observed frequencies are interpreted to indicate an upper level $n=+1$ and a lower level $n=-1$ with respect to a mean level of energy H_0. Strangely enough the ratio of upper (or lower) level energy H_n to mean level energy H_0 is of the order of 1/3 as against the 1/2 obtained from the Heisenberg–Born mechanics for E_0. Considerable freedom, however, is left open for specifying the "orbital frequency" of the generators.

The evidence goes to show that the postulates of the Quantum Mechanics do not necessarily involve such bold assumptions as appear to be the case at first sight. Part of their strange character seems to be due to the use of non-radiating harmonic oscillators, whereas those of the radiating type are now made mathematically available.

It is significant that it should be possible to show from purely classical considerations that the non-radiating harmonic oscillator is only then capable of becoming of radiating type when a discrete amount of energy (1/3 of the non-radiating content) is continuously being absorbed and re-radiated. This appears to suggest that the radiating harmonic oscillator of the text is analogous in its properties to that of an ordinary organ-pipe.

THE equation of the non-radiating harmonic oscillator is

$$H = \tfrac{1}{2}p^2 + 2\pi\nu_0^2 q^2, \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

where p is the generalized momentum and q is the generalized displacement. Consider, then, matrices of elements such as those of the Heisenberg–Born type:

$$q = (q_{mn}\epsilon^{2\pi i\nu(mn)t}); \quad p = (p_{mn}\epsilon^{2\pi i\nu(mn)t}) \dagger. \quad . \quad . \quad (2)$$

It is possible to get a correspondence between the matrices

* Attention should be directed to a very important contribution to the discussion and history of the Linear Oscillator by Prof. G. A. Schott F.R.S., in the Phil. Mag. for April 1927, p. 739.

† A different type of matrix will be further in question.

p and q and the true momenta and displacements p and q if we consider the following resultant matrix:

$$d=pq-qp=\mathrm{U}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus, let it be assumed that the process of differentiation with respect to the time can be performed in the following way:

$$\left(\frac{d}{dt}\right)d=\dot{d}=\left(\frac{d}{dt}\right)p\cdot q+p\cdot\left(\frac{d}{dt}\right)q-\left(\frac{d}{dt}\right)q\cdot p-q\cdot\left(\frac{d}{dt}\right)p,$$

$$\text{or} \qquad \dot{d}=\dot{p}q+p\dot{q}-\dot{q}p-q\dot{p}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Let it be further assumed that we can have a matrix function H analogous to H above, such that we can have corresponding canonical equations, viz.:

$$\frac{\partial \mathrm{H}}{\partial p}=\dot{q}\,; \quad -\frac{\partial \mathrm{H}}{\partial q}=\dot{p}. \quad . \quad . \quad . \quad . \quad (5)$$

It follows at once on substitution in (4) that

$$\dot{d}=-\frac{\partial \mathrm{H}}{\partial q}\cdot q+p\cdot\frac{\partial \mathrm{H}}{\partial p}-\frac{\partial \mathrm{H}}{\partial p}\cdot p+q\cdot\frac{\partial \mathrm{H}}{\partial q}$$

$$\dot{d}=\left\{q\cdot\frac{\partial \mathrm{H}}{\partial q}-\frac{\partial \mathrm{H}}{\partial q}\cdot q\right\}+\left\{p\cdot\frac{\partial \mathrm{H}}{\partial p}-\frac{\partial \mathrm{H}}{\partial p}\cdot p\right\}. \quad . \quad (6)$$

It can be shown quite generally in connexion with matrices that, adopting Dirac's Poisson-bracket notation *

$$-\left[\frac{\partial \mathrm{H}}{\partial q}\cdot q\right]=-q\frac{\partial \mathrm{H}}{\partial q}+\frac{\partial \mathrm{H}}{\partial q}q=\left[q\cdot\frac{\partial \mathrm{H}}{\partial q}\right]=\frac{\partial^2 \mathrm{H}}{\partial p\,\partial q},$$

whereas

$$\left[\frac{\partial \mathrm{H}}{\partial p}\cdot p\right]=p\cdot\frac{\partial \mathrm{H}}{\partial p}-\frac{\partial \mathrm{H}}{\partial p}\cdot p=\frac{\partial^2 \mathrm{H}}{\partial q\,\partial p}. \quad . \quad . \quad . \quad . \quad (7)$$

There can therefore be a correspondence between the canonical equations of Hamilton and the canonical equations of Heisenberg for matrices generally, provided that the matrices are such that

$$\dot{d}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This means that the matrices must be of the type that

$$pq-qp=\text{constant (independent of } t). \quad . \quad . \quad (9)$$

The above two conditions can be met, first by interpreting the multiplication of matrices so that the time functions should not appear. This implies that a special meaning needs to be given to "multiplication," for by (4) it is presumed that the p's and q's are in fact functions of the time. Secondly, in order to meet the condition (9), a diagonal matrix condition is necessary. This can also be

* See Appendix.

satisfied by properly interpreting the elements of the resultant multiplication matrix.

Let us therefore form matrices and then develop their products. Thus let, for example,

$$q=\begin{Bmatrix} q_{11} & q_{12} & q_{13} \\ q_{21} & q_{22} & q_{23} \\ q_{31} & q_{32} & q_{33} \end{Bmatrix}. \quad . \quad (10) \qquad p=\begin{Bmatrix} p_{11} & p_{12} & p_{13} \\ p_{21} & p_{22} & p_{23} \\ p_{31} & p_{32} & p_{33} \end{Bmatrix}. \quad . \quad (11)$$

$$pq=\begin{Bmatrix} (p_{11}q_{11}+p_{12}q_{21}+p_{13}q_{31}) & (p_{11}q_{12}+p_{12}q_{22}+p_{13}q_{32}) & (p_{11}q_{13}+p_{12}q_{23}+p_{13}q_{33}) \\ (p_{21}q_{11}+p_{22}q_{21}+p_{23}q_{31}) & (p_{21}q_{12}+p_{22}q_{22}+p_{23}q_{32}) & (p_{21}q_{13}+p_{22}q_{23}+p_{23}q_{33}) \\ (p_{31}q_{11}+p_{32}q_{21}+p_{33}q_{31}) & (p_{31}q_{12}+p_{32}q_{22}+p_{33}q_{32}) & (p_{31}q_{13}+p_{32}q_{23}+p_{33}q_{33}) \end{Bmatrix}. \quad (12)$$

$$qp=\begin{Bmatrix} (q_{11}p_{11}+q_{12}p_{21}+q_{13}p_{31}) & (q_{11}p_{12}+q_{12}p_{22}+q_{13}p_{32}) & (q_{11}p_{13}+q_{12}p_{23}+q_{13}p_{33}) \\ (q_{21}p_{11}+q_{22}p_{21}+q_{23}p_{31}) & (q_{21}p_{12}+q_{22}p_{22}+q_{23}p_{32}) & (q_{21}p_{13}+q_{22}p_{23}+q_{23}p_{33}) \\ (q_{31}p_{11}+q_{32}p_{21}+q_{33}p_{31}) & (q_{31}p_{12}+q_{32}p_{22}+q_{33}p_{32}) & (q_{31}p_{13}+q_{32}p_{23}+q_{33}p_{33}) \end{Bmatrix}. \quad (13)$$

It will be noticed that in pq, as well as in qp, the diagonal elements are either of the form

$$\Sigma p_{mn}q_{nm} \quad \text{or} \quad \Sigma q_{mn}p_{nm}. \quad . \quad . \quad . \quad . \quad (14)$$

The condition then needs to be imposed by definition that

$$p_{mn}q_{rs}=0 \text{ for } m\neq s\,;\ n\neq r. \quad . \quad . \quad . \quad (15)$$

The significance of this condition will be brought out later and will amount to ignoring term elements producing expressions in which the frequency of a p_{mn} element differs from the frequency of a q_{rs} element.

Forming now the subtraction of matrices (12) and (13), it is at once apparent that only diagonal elements need to be considered, and we have, subject to (15), that

$$pq-qp=\begin{Bmatrix} \{(p_{11}q_{11}-q_{11}p_{11})+(p_{12}q_{21}-q_{12}p_{21})+(p_{13}q_{31}-q_{13}p_{31})\} & 0 & 0 \\ 0 & \{(p_{21}q_{12}-q_{21}p_{12})+(p_{22}q_{22}-q_{22}p_{22})+(p_{23}q_{32}-q_{23}p_{32})\} & 0 \\ 0 & 0 & \{(p_{31}q_{13}-q_{31}p_{13})+(p_{32}q_{23}-q_{32}p_{23})+(p_{33}q_{33}-q_{33}p_{33})\} \end{Bmatrix}. \quad . \quad . \quad (16)$$

The general term of any diagonal element is therefore seen to be of the form of

$$\Sigma(p_{mn}q_{nm}-q_{mn}p_{nm}). \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The multiplication of matrices has then to be so limited by definition that an expression such as (17) has no longer to involve the time function *per se*. It will then result that the canonical equations of classical mechanics can be translated in invariant form into the domain of general matrix mechanics. The first important thing, then, in a rationalization of matrix mechanics is to give a physical basis for the interpretation of (17).

By a theorem in classical generalized mechanics already deduced by the writer (see Phil. Mag. Sept. 1924), it was proved that if we have a component of generalized force defined by

$$\left.\begin{aligned} \mathrm{E}(mn) &= \mathrm{E}_{nm}\sin\omega t + \mathrm{E}_{mn}\cos\omega t, \\ \text{and a consequent generalized displacement} \quad & \\ \mathrm{D}(mn) &= \mathrm{D}_{nm}\sin\omega t + \mathrm{D}_{mn}\cos\omega t, \end{aligned}\right\} \quad . \quad . \quad . \quad (18)$$

the rate of doing work depended on the expression

$$\mathrm{E}(mn)\,.\,\frac{d}{dt}\mathrm{D}(mn) = \omega[\{\mathrm{E}_{mn}\mathrm{D}_{nm}-\mathrm{D}_{mn}\mathrm{E}_{nm}\}\cos^2\omega t + \mathrm{E}_{nm}\mathrm{D}_{mn}\cos 2\omega t + \tfrac{1}{2}(\mathrm{E}_{nm}\mathrm{D}_{nm}-\mathrm{D}_{mn}\,.\,\mathrm{E}_{mn})\sin 2\omega t]. \quad (19)$$

For a real activity (Force × Velocity of Displacement) therefore, it is required that

$$\mathrm{E}_{mn}\mathrm{D}_{nm}-\mathrm{D}_{mn}\,.\,\mathrm{E}_{nm}\neq 0. \quad . \quad . \quad . \quad . \quad (20)$$

The $2\omega t$ terms can contribute nothing to the real average activity. A similar expression will be developed for the action $p\ (mn)\,.\,q\ (nm)$, and will be used for the interpretation of (17). One thing is certain, from (20) we can never have an expression

$$\frac{\mathrm{D}_{mn}}{\mathrm{E}_{mn}} = k = \frac{\mathrm{D}_{nm}}{\mathrm{E}_{nm}}, \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where k has an ordinary real scalar value. Expression (20) would under those circumstances reduce to zero, which is contrary to hypothesis. In other words, $\mathrm{E}(mn)$ and $\mathrm{D}(mn)$ must, for real activity, be out of phase to some degree at least, and we should write instead

$$\mathrm{D} = k\mathrm{E}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where $\dot{k}$ for complex operands is also complex *. That is, let

$$\dot{k} = k_1 - k_2 j \dagger, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

then with

$$\dot{D}(mn) = (D_{nm} + D_{mn}j) \cdot \sin \omega t, \quad . \quad (24)$$

$$\left.\begin{aligned}(k_1 - k_2 j)\dot{E}(mn) &= (D_{nm} + D_{mn}j) \cdot \sin \omega t \\ \dot{E}(mn) &= (E_{nm} + E_{mn}j) \cdot \sin \omega t\end{aligned}\right\} \quad . \quad (25)$$

We have, by definition for the work done,

$$dW = \dot{E} \cdot d\dot{D} = \dot{E}\, dt \cdot \frac{d\dot{D}}{dt} = \dot{D} \cdot d\dot{P} = \frac{d\dot{P}}{dt} \cdot d\dot{D}. \quad . \quad (26)$$

This follows, because for a generalized momentum $\dot{P}$ the following obtains:

$$\frac{d\dot{P}}{dt} = \dot{E}; \quad \dot{P} = \int \dot{E} \cdot dt. \quad . \quad . \quad . \quad . \quad (27)$$

Yet it is to be borne in mind that with

$$\frac{d}{dt} = \omega j, \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

$$\dot{E} = \frac{\dot{D}}{\dot{k}} = \frac{d\dot{P}}{dt} = \omega j \dot{P}, \quad . \quad . \quad . \quad . \quad (29)$$

showing that the generalized momentum $\dot{P}$ cannot be in time-phase with $\dot{D}$. To deduce the latter we have

$$\dot{P} = \frac{\dot{D}}{k\omega j} = -\frac{1}{\omega^2} \cdot \frac{1}{\dot{k}} \cdot \frac{d\dot{D}}{dt} = \frac{-(k_1 + k_2 j)}{\omega^2 k^2} \cdot \frac{d\dot{D}}{dt} \ddagger, \quad (30)$$

where we define for convenience that

$$k^2 = k_1^2 + k_2^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

A relation corresponding to (19) can be obtained for pq

* By $\dot{k}$ being complex is meant that a component $k_1\dot{E}$ of $\dot{D}$ is in time-phase with $\dot{E}$, but the component of magnitude $k_2\dot{E}$ of $\dot{D}$ is in time-quadrature with respect to $\dot{E}$. The Heaviside–Perry method of complexes, or Resistance Operators, was first extensively treated in Perry's 'Calculus for Engineers' (see pp. 236 *et seq.*). The method is much more powerful than that of Steinmetz, since the latter has to do with the effective values of the variables, whereas the Heaviside operational method deals with instantaneous values throughout—an all important difference.

† See author's "Harmonic Algebra," Univ. of Calif. Pubn's. Sept. 30, 1919. Also Heaviside, Elec. Mag. Theory, vol. ii. p. 228.

‡ This important result will be employed in developing the differential equation of a Radiating Harmonic Oscillator.

by noting first that

$$\frac{d\mathrm{D}(mn)}{dt} = \omega(\mathrm{D}_{nm}\cos\omega t - \mathrm{D}_{mn}\sin\omega t) \quad . \quad . \quad (32)$$

$$\mathrm{E}(mn) = \mathrm{E}_{nm}\sin\omega t + \mathrm{E}_{mn}\cos\omega t. \quad . \quad . \quad . \quad (33)$$

It is the multiplication of the right-hand expressions that leads to (19). For (32), (33), we can therefore substitute

$$\left.\begin{aligned} p(mn) &= (\omega p'_{nm})\cos\omega t - (\omega p'_{mn})\sin\omega t \\ q(mn) &= q_{nm}\sin\omega t + q_{mn}\cos\omega t \end{aligned}\right\} \quad . \quad . \quad (34)$$

These should lead to a form similar to (19) by using the substitution $\omega p'$ for D_{nm} and q_{nm} for E_{nm}, etc. However, if instead we write

$$p(mn) = p_{nm}\cos\omega t - p_{mn}\sin\omega t, \quad . \quad . \quad . \quad (35)$$

the result will be

$$p(mn)\,.\,q(mn) = [(q_{mn}p_{nm} - p_{mn}q_{nm})\cos^2\omega t + q_{nm}p_{mn}\cos 2\omega t + \tfrac{1}{2}(q_{nm}p_{nm} - p_{mn}q_{mn})\sin 2\omega t]. \quad . \quad . \quad . \quad (36)$$

The mean action would thus depend on the expression

$$p_{mn}q_{nm} - q_{mn}p_{nm} = \mathrm{B} \neq 0, \quad . \quad . \quad . \quad . \quad (37)$$

which will be plus or minus depending on whether radiation of energy or absorption exists. Expression (37) indicates in what manner the matrices for p and q are to be built u and moreover, indicates in what manner matrix multiplication is to be understood, and more especially wi regard to d or U of (3).

Given that to each generator of a radiating system S are to be allocated a displacement coordinate $q(mn)$ and a momentum coordinate $p(mn)$, with reference to a unit or standard aggregation of generators (time t=zero) acting as reference, then the two expressions are to be written in the form

$$q(mn) = q_{nm}\sin 2\pi\nu(mn)t + q_{mn}\cos 2\pi\nu(mn)t. \quad . \quad (38)$$

$$p(mn) = -p_{mn}\sin 2\pi\nu(mn)t + p_{nm}\cos 2\pi\nu(mn)t. \quad (39)$$

For simplicity we can write

$$q(mn) = (q_{nn} + q_{mn}j)\sin 2\pi\nu(mn)t = q_{nm}s_{mn} + q_{mn}c_{mn} = q(nm) + q(mn), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

and for the momentum function

$$p(mn) = (-p_{mn} + p_{nm}j)\sin 2\pi\nu(mn)t = -p_{mn}c_{mn} + p_{nm}c_{mn} = -p(mn) + p(nm). \quad . \quad (41)$$

Writing out the matrix expressions for the S-system, we then have, for example,

$$p=\begin{Bmatrix} p(11)\ p(12)\ p(13) \\ p(21)\ p(22)\ p(23) \\ p(31)\ p(32)\ p(33) \end{Bmatrix}; \quad q=\begin{Bmatrix} q(11)\ q(12)\ q(13) \\ q(21)\ q(22)\ q(23) \\ q(31)\ q(32)\ q(33) \end{Bmatrix}. \quad (42)$$

Proper regard must, however, be paid to the fact that whereas any $q(mn)$ in q of (42) corresponds to the cosine function, such that

$$q(mn)=q_{mn}\cos 2\pi\nu(mn)t,$$

the $p(mn)$ of p corresponds to the sine function, so that

$$p(mn)=-p_{mn}\sin 2\pi\nu(mn)t.$$

In a similar way the following values hold:

$$q(nm)=q_{nm}\sin 2\pi\nu(mn)t\ ; \quad p(nm)=p_{nm}\cos 2\pi\nu(mn)t.$$

For convenience, we can set that

$$\nu(mn)=-\nu(nm). \quad . \quad . \quad . \quad . \quad . \quad (43)$$

We can then write

$$\left.\begin{aligned} q(mn)&=q_{mn}\cos 2\pi\nu(mn)t \\ q(nm)&=q_{nm}\sin 2\pi\nu(mn)t \end{aligned}\right\}. \quad . \quad . \quad . \quad (44)$$

$$\left.\begin{aligned} p(mn)&=p_{mn}\sin 2\pi\nu(nm)t \\ p(nm)&=p_{nm}\cos 2\pi\nu(nm)t \end{aligned}\right\}. \quad . \quad . \quad . \quad (45)$$

It is then the multiplication of two matrices of the form (10) and (11) rather than (42) that will give the resultant d according to (44) and (45), viz.:

$$pq-qp$$

$$=\begin{Bmatrix} \{(p_{11}q_{11}-q_{11}p_{11})+(p_{12}q_{21}-q_{12}p_{21}) & & \\ \quad +(p_{13}q_{31}-q_{13}p_{13})\} & 0 & 0 \\ 0 & \{(p_{21}q_{12}-q_{21}p_{12})+(p_{22}q_{22}-q_{22}p_{22}) & \\ & \quad +(p_{23}q_{32}-q_{23}p_{23})\} & 0 \\ 0 & 0 & \{(p_{31}q_{13}-q_{31}p_{13})+(p_{32}q_{23}-q_{32}p_{23}) \\ & & \quad +(p_{33}q_{33}-q_{33}p_{33})\} \end{Bmatrix}$$

$$. \quad . \quad (46)$$

A simplified form of the bracket values represented by $p_{mn}q_{nm}-q_{mn}p_{nm}$ in (46) will now be in order.

It has already been pointed out in (30) that the generalized momentum P can be expressed in terms of the generalized displacement D and of $\dot{\mathrm{D}}$. We have, in fact, that

$$\mathrm{P}=\frac{\mathrm{D}}{k\omega j}=\frac{k_1+k_2 j}{\omega j k^2}(\mathrm{D}_1+\mathrm{D}_2 j)\sin\omega t. \quad . \quad . \quad (47)$$

It follows, therefore, that

$$k^2\omega \mathrm{P} = (k_2 - k_1 j)(\mathrm{D}_1 + \mathrm{D}_2 j) \sin \omega t$$
$$= (k_2 \mathrm{D}_1 + k_1 \mathrm{D}_2)s + (\mathrm{D}_2 k_2 - k_1 \mathrm{D}_1)c \text{ *}. \quad . \quad (48)$$

Thus multiplying through with D to obtain the action, we have

$$k^2\omega \mathrm{PD} = [(k_2\mathrm{D}_1 + k_1\mathrm{D}_2)s + (\mathrm{D}_2 k_2 - \mathrm{D}_1 k_1)c](\mathrm{D}_1 s + \mathrm{D}_2 c)$$
$$= \{\mathrm{D}_1(k_2\mathrm{D}_1 + k_1\mathrm{D}_2)\sin^2 \omega t + \mathrm{D}_2(\mathrm{D}_2 k_2 - \mathrm{D}_1 k_1)\cos^2 \omega t\}$$
$$+ \{\mathrm{D}_1(\mathrm{D}_2 k_2 - \mathrm{D}_1 k_1) + \mathrm{D}_2(k_2\mathrm{D}_1 + k_1\mathrm{D}_2)\} \sin \omega t \,.\, \cos \omega t.$$
$$. \quad . \quad . \quad (49)$$

It thus appears the average value of the action depends on the expression

$$\frac{1}{2\pi}\oint \mathrm{PD}\,dt = [\mathrm{PD}]_{\text{av.}} = \left\{\frac{1}{2}\frac{(\mathrm{D}_1^2 + \mathrm{D}_2^2)}{\omega^2_{mn}} \cdot \frac{2\pi k_2}{k^2}\right\}\frac{1}{2\pi}. \quad (50)$$

Translated into the notation of (36), therefore, we have by (38) that

$$p(mn)\,.\,q(mn)\,]_{\text{av.}} = q_{mn}p_{nm} - p_{mn}q_{nm}$$
$$= \left\{\frac{2\pi k_2}{k^2}\cdot\frac{1}{2}\cdot\frac{(q^2_{mn} + q^2_{nm})}{\omega^2_{mn}}\right\}\frac{1}{2\pi} = \left\{\frac{\pi k_2}{k^2}\frac{|\,q(mn)\,|^2}{\omega^2_{mn}}\right\}\frac{1}{2\pi}. \quad (51)$$

The latter brings out an analogy with the postulate of the quantum theory, for we can write (instead of h/i),

$$\chi_{mn} = \frac{\pi k_2}{\omega^2_{mn}k^2}(q^2_{mn} + q^2_{nm})\,\dagger, \quad . \quad . \quad . \quad (52)$$

where χ_{mn} would be a constant for an observation steady state. In any event (51) and (52) do not contain the time. There is then justification in regarding U of (3) as a "unit" matrix.

The following rule can therefore be enunciated. In forming a matrix product of elements the ordinary multiplication rule of algebraic matrices is understood, but in addition it is implied that average or mean time values be inserted in the resultant. As to differentiation with respect to time, it means that the differential of the resultant matrix is the same as the differential with regard to the individual matrices comprising the operand originally, and then taking average time values.

* Here s is employed for $\sin \omega t$ and c for $\cos \omega t$. When dealing with the double periodicity terms, as in the product PD of (49), the operators must be translated into c's, and appropriate s's introduced for the terms involving the sine functions of the time.

† A later improved form will be shown to involve the momenta rather than the coordinates divided by the frequency.

It is at once apparent from (26) that the amount of work done, as by radiation, can be put into two forms :

$$dW = \dot{D} \cdot dP \; ; \quad dW = \dot{P} \cdot dD,$$

indicating that W must be a function of P, $\dot{P}$, D, $\dot{D}$. If, then, by partial differentiation it is understood that

$$dW = \frac{\partial W}{\partial D} dD + \frac{\partial W}{\partial P} dP, \quad . \quad . \quad . \quad . \quad (53)$$

then this will lead to a solution

$$W = f(P, D), \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

provided that no $\dot{P}$'s or $\dot{D}$'s are presumed to appear in the last equation. If they are to appear at all they must do so by substitution only in the partial derivatives

$$\left.\begin{aligned} \frac{\partial W}{\partial D} &= \dot{P} \\ \frac{\partial W}{\partial P} &= \dot{D} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

The latter equations expressing radiation conditions, as a system, are more symmetrical even than the analogous Hamiltonian equations.

Transposing to the notation (5) we have for matrices

$$\frac{\partial W}{\partial q} = \dot{p} \; ; \quad \frac{\partial W}{\partial p} = \dot{q}, \quad . \quad . \quad . \quad . \quad (56)$$

with the reservation, as known from (30), that p is not in phase with $\dot{q}$. In fact, from (34), we have

$$\left.\begin{aligned} q(mn) &= (q_{nm} + jq_{mn}) \sin \omega t \; ; \\ \dot{q}(mn) &= \omega j (q_{nm} + q_{mn} j) \sin \omega t \end{aligned}\right\} \quad . \quad . \quad . \quad (57)$$

On the other hand, from (30), we also note that

$$\dot{p}(mn) = - \frac{k_1 + k_2 j}{\omega^2 k^2} \cdot \frac{dq}{dt} \quad . \quad . \quad . \quad . \quad (58)$$

Thus

$$\dot{p}(mn) = - \frac{1}{\omega^2 k^2} \left\{ \frac{k_2}{\omega} \cdot \frac{d}{dt} + k_1 \right\} \dot{q}, \quad . \quad . \quad (59)$$

$$\dot{p}(mn) = - \frac{k_1}{\omega^2 k^2} \dot{q} - \frac{k_2}{\omega^3 k^2} \ddot{q}. \quad . \quad . \quad . \quad . \quad (60)$$

To develop the differential equation for the Radiating Harmonic Oscillator, the Hamiltonian canonical equations are

$$\frac{\partial H}{\partial p} = \dot{q} \; ; \quad - \frac{\partial H}{\partial q} = \dot{p}. \quad . \quad . \quad . \quad . \quad (61)$$

It was the above equations that were made the basis of

treatment for the Matrix Mechanics. We have, however, seen by (30) that as a condition for real activity (or action) we must have that

$$-\frac{\omega^2 k^2}{k_1 - k_2 j} \cdot p = \dot{q}. \quad \ldots \ldots \quad (62)$$

This gives a clue for the *possible* form of H. Thus by combining (61) and (62), we have

$$\frac{\partial \underline{H}}{\partial \underline{p}} = -\omega^2(k_1 - k_2 j)\underline{p} = -\omega^2 k_1 \underline{p} + k_2 \omega \frac{d\underline{p}}{dt}$$
$$= -\omega^2 k_1 \underline{p} + k_2 \omega \dot{\underline{p}}. \quad \ldots \ldots \quad (63)$$

On integrating the last equation, it follows

$$\underline{H} = -\frac{\omega^2 k_1}{2}\underline{p}^2 + k_2 \omega \dot{\underline{p}}\underline{p} + f(\underline{q}). \quad \ldots \quad (64)$$

Applying now the second equation of (61) it is seen that

$$-\frac{\partial \underline{H}}{\partial \underline{q}} = \dot{\underline{p}} = \frac{\partial}{\partial \underline{q}} f(\underline{q}), \quad \ldots \ldots \quad (65)$$

whence integrating, the form of $\underline{H}$ must be

$$\underline{H} = -\frac{\omega^2 k_1}{2}\underline{p}^2 + k_2 \omega \underline{p}\dot{\underline{p}} - \dot{\underline{p}}\underline{q}. \quad \ldots \quad (66)$$

It is the latter equation and not (1) that applies to the problem of radiating systems.

Taking now the case of equation (30), we have, dropping subscripts,

$$p = \frac{q}{k\omega j}; \quad \dot{q} = (k_1 - k_2 j)\omega j \dot{p}. \quad \ldots \quad (67)$$

If, then, for convenience, we let

$$p = \mathrm{P} \sin \omega t', \quad \ldots \ldots \quad (68)$$

$$q = \omega \mathrm{P}(k_1 c + k_2 s) \quad \ldots \ldots \quad (69)\ *$$

This means that

$$\dot{p} = \omega j \mathrm{P} \sin \omega t' = \omega \mathrm{P} c, \quad \ldots \ldots \quad (70)$$

$$\dot{p}q = \omega^2 \mathrm{P}^2(k_1 c^2 + k_2 sc). \quad \ldots \ldots \quad (71)$$

Turning now to the next to the last term in (66), we likewise have

$$p\dot{p} = \mathrm{P}s\omega \mathrm{P}c = \omega \mathrm{P}^2 sc,$$

so that on multiplying with $k_2\omega$, we have

$$k_2 \omega p\dot{p} = k_2 \omega^2 \mathrm{P}^2 sc. \quad \ldots \ldots \quad (72)$$

* From (68) and (69) we note that for the absolute value $|p|^2 = \mathrm{P}^2$, whereas $|q|^2 = \omega^2 \mathrm{P}^2 k^2$. In other words $|\dot{q}|^2 = 4\pi^2 \nu^2 k^2 |p|^2$. This is the result of (77).

The remaining term gives

$$p^2 = \mathrm{P}^2 s^2,$$

$$\frac{\omega^2 k_1}{2} p^2 = \omega^2 \mathrm{P}^2 \frac{k_1}{2} s^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (73)$$

Now, adding all the terms together, it follows that

$$-\mathrm{H} = \omega^2 \mathrm{P}^2 \left\{ \frac{k_1}{2} s^2 + k_1 c^2 \right\}$$

$$= \tfrac{3}{4} \omega^2 \mathrm{P}^2 k_1 \{ 1 + \tfrac{1}{3} \cos 2\omega t' \}. \quad . \quad . \quad . \quad (74)$$

The latter equation it is seen indicates a constant component for the total energy $\underline{\mathrm{H}}$, which is given by

$$-\mathrm{H}_0 = \tfrac{3}{4} \omega^2 \mathrm{P}^2 k_1. \quad . \quad . \quad . \quad . \quad . \quad (75)$$

This type of term means *no radiation*. Such radiation as does appear must come from the variable remainder represented by

$$-\mathrm{H}_v = \tfrac{1}{4} \omega^2 \mathrm{P}^2 k_1 . \cos 2\omega t'. \quad . \quad . \quad . \quad . \quad (76)$$

The amplitude of the radiation is seen to fluctuate about a mean level H_0 of (75) with equal ranges (energy levels) plus and minus. This accords with the Heisenberg–Born Matrix Condition $n = \pm 1$. In (76) such amplitude has preferably been expressed in terms of the square of the momentum and the frequency.

To transform (76) as well as condition (52) use can be made of (69), which gives

$$|q|^2 = \omega^2 \mathrm{P}^2 k^2 = \omega^2 k^2 |p|^2, \quad . \quad . \quad . \quad . \quad (77)$$

yet it is better to refer to the momenta amplitudes rather than the coordinate ones in order to emphasize the analogies with the quantum theory. We then have that

$$\chi = \frac{\pi}{2} k_2 \mathrm{P}^2 = \frac{\pi}{2} k_2 |p|^2, \quad . \quad . \quad . \quad . \quad (78)$$

which is of the order of an energy (or quantum).

The ratio of the two energies above is given by

$$\frac{\mathrm{H}}{\mathrm{H}_0} = \frac{1}{3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (79)$$

It is significant that H_0 corresponds to the constant aggregate energy of the non-radiating harmonic oscillator heretofore employed, whereas H_v represents the amplitude of the fluctuating absorption and radiating component. Nothing is indicated about the "orbital periodicity" with which the potential and kinetic energies interchange in the

H_0 system. Whether there is a relationship of this latter with the half frequency component of the Nernst–Lindemann formula has yet to be determined, at least it is suggestive. In any case one thing is certain, equation (79) has been arrived at on purely classical lines, and it shows as a consequence of applying Hamilton's canonical equations that an unexcited harmonic oscillator, when caused to radiate by virtue of an impressed field of force, only then becomes radiating when it can absorb and re-radiate a definite discrete quantum of energy equal to 1/3 of its normal unexcited content. This corresponds exactly with one of the conditions of the Planck–Bohr developments.

Indeed, an harmonic oscillator of the organ-pipe type does not give an appreciable increase of volume with increased blowing pressure. A point is soon reached when the dominant frequency takes a discrete jump in conformity with Bohr requirements.

Appendix.

Employing the bracket notation of Dirac, let

$$pq - qp = [q, p] = \mathrm{U},$$
$$-[q, p] = [p, q].$$

To interpret $[q, p^2]$, we note

$$[q, p^2] = p^2q - qp^2 = p(pq) - (qp)p = p(pq - qp) + (pq - qp)p$$
$$= p\mathrm{U} + \mathrm{U}p = 2p \,.\, \mathrm{U}.$$

In a similar manner it can be shown that

$$[q^2, p] = 2q\mathrm{U},$$

indicating quite generally

$$[q, p^n] = np^{n-1} \,.\, \mathrm{U} = \frac{\partial}{\partial p} p^n.$$

$$[q^n, p] = \frac{\partial}{\partial q} q^n.$$

In fact, as a simple extension for functions of q and p expressible as a series, we should have, dropping the unity matrix, that

$$[F(p, q), p] = \frac{\partial F}{\partial q}; \quad [q, \mathrm{F}(p, q)] = \frac{\partial \mathrm{F}}{\partial p}.$$

* Kind acknowledgements are made to Dr. A. S. Eve, Director of the Physics Department of McGill University, to Professor A. H. S. Gillson, and to Dr. J. S. Foster, for their interest and criticisms.

CXI. *On the Behaviour of Small Quantities of Radon at Low Temperatures and Low Pressures.* *By* Alois F. Kovarik, *Ph.D., D.Sc., Professor of Physics, Yale University* *.

THE temperature at which radon condenses or volatilizes was first investigated by Rutherford and Soddy †. They found that radon commences to volatilize at 120° absolute in their experiments in which a current of gas passed through the apparatus, and at 123° absolute in a stationary atmosphere. Boyle ‡, using the flow method, found the volatilization temperature at about 113° absolute. Laborde § found the same temperature of volatilization 120° to 122° absolute in spirals of copper, iron, tin, and silver, but about 20° lower in glass; Boyle's experiments, however, did not show any material difference for the metals and glass. Boyle and others have observed that radon at liquid-air temperature exhibits a vapour pressure, and Rutherford ‖ was the first to measure the vapour pressure when radon condensed to form a liquid. This was later also done by Gray and Ramsay ¶. In these experiments large quantities of radon were used and a liquid radon was observed. Several observers, using small quantities of radon, have observed variations in the vapour pressure as a function of the quantity of radon used. The first of these observations are recorded by Russ and Makower ** and by Boyle ††, and more recently by Fleck ‡‡ in his investigations of the condensation temperatures of radon and thoron. While Boyle's experiments bear out the general conclusion that a vapour phase of radon exists at any temperature, the numerical results were found to be irregular. It is also to be pointed out that since radon and thoron are isotopes, the temperatures of volatilization of radon and thoron should be the same; the problem was attacked by Fleck.

Rutherford, in his 'Radioactive Substances and their Radiations,' discusses these problems in some detail. Recently, while enjoying the hospitality of Cambridge

* Communicated by Prof. Sir E. Rutherford, O.M., P.R.S.

† Rutherford & Soddy, Phil. Mag. v. p. 561 (1903).

‡ Boyle, R. W., Phil. Mag. xx. p. 955 (1910).

§ Laborde, *Le Radium*, vi. p. 289 (1909); vii. p. 294 (1910).

‖ Rutherford, E., 'Nature,' lxxix. p. 457 (1909); Phil. Mag. xvii. p. 723 (1909).

¶ Gray & Ramsay, Trans. Chem. Soc. xcv. p. 1073 (1909).

** Russ & Makower, Proc. Roy. Soc. A, lxxxii. p. 205 (1909).

†† Boyle, R. W., Phil. Mag. xxi. p. 722 (1911).

‡‡ Fleck, A., Phil. Mag. (6) xxix. p. 337 (1915).

and the Cavendish Laboratory, the writer found Rutherford still much interested in these problems, and at his suggestion attempted the research which finally took the form embodied in this paper, and which is, briefly, an attempt to measure the vapour pressures of small quantities of radon at low temperatures under conditions of low pressure in the apparatus. Preliminary experiments were also carried out on the volatilization temperature under similar conditions of low pressure and small quantities of radon. Some experiments on the vapour pressure were repeated, extending the range of temperature, on my return to Yale.

From what we know of the equilibrium relations between the vapour-liquid and vapour-solid phases in the case of ordinary substances, we are forced to conclude that similar relations should hold in the case of radon, as indeed was shown for the vapour-liquid equilibrium by Rutherford and by Gray and Ramsay. When small quantities of radon are used, we cannot conclude that the condensed phase is either liquid or solid, for it is possible that it may be a condensation of single atoms into a layer which may not be even monatomic. In the latter case the work function may be quite different; and if the energy of "volatilization" of atoms of radon from a surface of glass should be greater than from solid radon, then the pressure of the radon vapour may be considerably smaller in the former case. The results of these experiments indicate this to be the case, but they also suggest that some radon may, at a very low temperature, also be solid radon, and that in different experiments the conditions for such dual condensation may vary, thus explaining the various irregularities that have been heretofore observed. In such a case one would expect that if sufficient time elapsed after the condensation took place, the phase with a higher vapour pressure would pass into the phase of lower pressure before real equilibrium was established. This, however, may not be observed in the ordinary procedure of the experiments. The observations are given in detail as the results may be found to have theoretical significance, for, if radon atoms could be condensed singly, the question arises whether or not the forces holding the atoms should be necessarily great since radon is inert and the explanations * of such forces in case of ordinary elements is based on action of valence electrons.

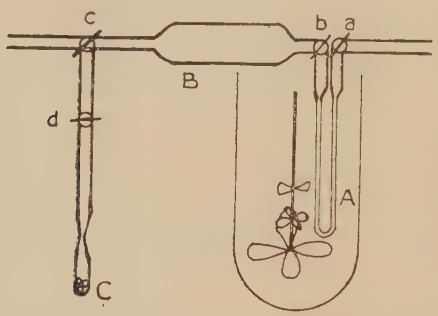
* Compare Langmuir, I., Am. Chem. Soc. Journ. xl. p. 1361 (1918).

Method and Apparatus.

Briefly the method of procedure to find the vapour pressure of radon at any temperature was as follows. Radon was condensed at liquid-air temperature in one part of the apparatus, which was then exhausted to a fairly low pressure. The radon was then subjected to a temperature desired, and after keeping it at this temperature for some time, it was allowed to diffuse into a known volume until a steady state was reached. The gaseous radon in the known volume was then collected in a charcoal tube immersed in liquid air. Similarly, the rest of the radon used was also collected. Later, the amounts of radon collected were measured, and from these measurements the pressure of the radon in the known volume was determined ; and by using Knudsen's relation of pressures at different temperatures in the same vessel, the pressure at the experimental temperature was deduced.

The essential parts of the apparatus are shown in fig. 1.

Fig. 1.



A was a U-shaped tube of 0·336 cm. internal diameter, having Failla internally-sealed vacuum stop-cocks at the two ends. Radon was condensed in A. Through one of the stop-cocks, *a* (of large bore), radon was admitted into A ; through the other, *b*, it could be allowed to diffuse into B, which in some experiments included the tubing *cd*. One arm of the three-way stop-cock, *c*, led to C through the stop-cock, *d*. C contained a small quantity of coconut shell charcoal, above which was a constricted portion of the tube for sealing-off purposes. When C was in the liquid-air bath the radon in B could be collected. Similarly, the radon in A—after removing A from its bath—could be collected into another similar tube, C, attached for this purpose. The third outlet from the three-way stop-cock led

to a rapidly-evacuating pump, a mercury pump, McLeod gauge, Plücker tube gauge, P_2O_5 bulbs, and charcoal bulbs used for evacuation purposes.

During an experiment, A was placed in a bath of pentane or of ligroïne (petroleum ether) contained in a pyrex glass tube, part of which extended into liquid air. The bath was kept constantly stirred. In some experiments this stirrer moved up and down about the U-shaped tube A, and in other experiments it was made of vanes on a rotating rod, two sets of vanes on the side of A being small and larger ones below A. A thermocouple of copper and constantan having one junction on the side of the lower part of A and the other in melting ice was used to measure the temperature.

The procedure in an experiment was as follows. The apparatus was exhausted and the radon was transferred by means of mercury into the apparatus, and by diffusion passed over P_2O_5 through the stop-cock *a* into A, the other stop-cock, *b*, being closed and A being immersed in liquid air. After about twenty minutes *a* was closed, *b* was opened, and *c* turned to shut off C, but allowing connexion with the pumps and gauges. By means of pumps the uncondensed gases with some radon were collected over mercury so as not to contaminate the laboratory with free radon. Exhaustion was carried on to a pressure of about 2 to 5×10^{-6} mm. Hg, and then the U-tube was closed off. Charcoal bulbs in liquid air in the pump-gauge system were then used to clear the vessel B of all radon. These charcoal bulbs were then closed, and the three-way stop-cock was turned to shut off the pumps, leaving B with *cd* connected or leaving B alone. A was now placed in its bath of ligroïne, and the desired temperature * of the bath was obtained by regulating the amount of immersion into liquid air, the stirrer being in operation. The temperature was read from the calibrated thermocouple, but an accurate pentane thermometer was always also used in the bath. After every experiment the temperature of boiling oxygen was obtained by the thermometers for checking purposes. When a desired temperature was kept constant for half an hour, A was connected to B, and the bath was kept continually at the desired temperature for another half-hour, after which A was again closed off. By trials it was found that one half-hour was sufficient time at the pressures used to get into what seemed to be an equilibrium state between A and B, as shown by the

* Bath for the very low temperatures was liquid air alone either freshly prepared or older.

fact that in a longer period no greater amount of radon apparently was diffused into B.

C having been previously heated and evacuated was now put into liquid air and the connecting stop-cocks with B opened. Fifteen minutes was sufficient to collect the radon from B. While C was in liquid air it was sealed off. Another similar charcoal tube was sealed on, and the tube was heated and evacuated and made ready to collect the radon remaining in A. The time of the experiment was noted so as to be able to calculate the amounts of radon at the time of the experiment. The amount of radon was determined by γ-ray measurements with the following apparatus, which was found admirable for comparisons of any quantities. A large size cylindrical can, 64 cm. long and 44 cm. diameter, was fitted out as an ionization vessel. Along the axis was a lead tube of 1 cm. thickness and having an axial opening large enough to allow the introduction of the specimen to be tested or the radium standard to be used in the calibration. In this way the ionization was produced by γ-rays after passing through 1 cm. of lead. Half-way between the lead tube and the walls of the can was a cylindrical electrode of sheet iron, which was connected to an electroscope. Owing to the great length of the cylinder, the slight variations in the size of the specimens (the charcoal radon tubes) made no difference, and in fact a displacement of these from the middle point by as much as 2 cm. could not be detected in the ionization readings. Several hours after the charcoal radon tubes were sealed, measurements were made, several in number extending over several days; and in each case the instrument was standardized by taking measurements of the ionization current when one of three radium standards (0·15 mg., 1·305 mg., 5·00 mg.) was put in the middle of the lead tube, using in any particular case that standard which most nearly coincided with the γ-radiation effect of the radon tubes. All readings for a given specimen were extrapolated to zero time and averaged. The result is the amount of radon in curies collected in each case. The results for the various experiments are given in columns 2 and 5 (Table I.).

Precautions and Criticisms.

It might be supposed that the radon gas may be occluded on the walls of the glass tubes leading to the charcoal bulb, and that in this manner some radon would be lost and not be collected in the charcoal tube. This

was tested by filling the apparatus with about 16 millicuries of radon at the usual low pressure, A being initially at liquid-air temperature, and after reduction of pressure both A and B being brought to room temperature. The radon was left in the apparatus for two hours, after which it was collected in the usual way, and a new tube was sealed on and evacuated, A and B having been closed off during this process. The pump-gauge system was then closed off and A and B were connected to C, which was in liquid air and was collecting any residual gas. All the glass tubes were heated for half an hour by a Bunsen burner up to as high a temperature as possible without causing a caving-in at any place. C was sealed off, and measurements on it showed a trace of radon, but only of a magnitude comparable to the natural leak of the measuring apparatus. Consequently, no appreciable amount of radon could be lost by occlusion to the walls of the apparatus.

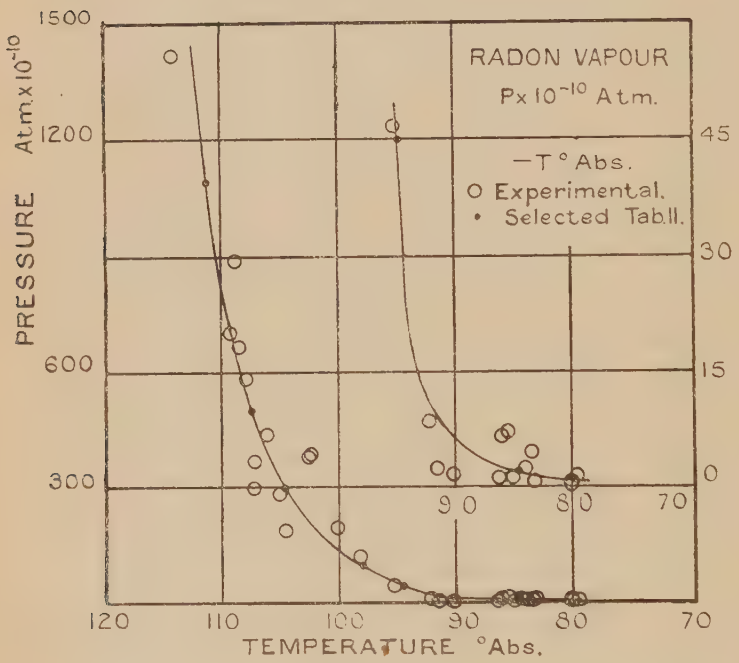
While the stop-cocks *a*, *b*, *c* were mercury sealed and graphite was used as a lubricant in most of the later experiments, small amounts of stop-cock grease of low vapour pressure were used in the first experiments. It is generally believed that radon is absorbed by the grease. Experiments were tried with large amounts of stop-cock grease put into the apparatus and exposed to 20 millicuries of radon for an hour. After collecting the radon and opening the apparatus, and collecting most of the grease so exposed and putting it along with the collectors (cleaners) into a test-tube and sealing it, it was found that the activity at the beginning was all due to radioactive deposit produced from the radon while this was in contact with it, and that after six hours a mere trace of activity could be detected. Consequently, in those experiments in which stop-cock grease was used no appreciable amount could have been lost by absorption by the grease.

Experiments were also tried to find the time necesssary to collect in C all the radon in B. It was found that no residual radon could be collected from B after C had been collecting for ten minutes, even when one hour was allowed to collect any possible residual radon. It seems, therefore, that whatever gaseous radon was in the apparatus from which it was collected by C was for all practical purposes collected, and that the amount found in the charcoal collecting-tube represents the amount dealt with in the experiment. It would seem, therefore, that the radon in B which during an experiment was in apparent equilibrium with the radon in A was for all practical purposes all

collected in C. The determination of its quantity by the ionization method was certainly the most accurate part of the experiment.

The galvanometer used in connexion with the thermo-couples gave a deflexion of the order of 4 divisions per degree, and each division could be estimated to at least one-fifth part. The actual temperature determinations were certainly correct to 1° centigrade, yet it will be noticed

Fig. 2.



from the curve (fig. 2) that the points do not lie on a smooth curve. The reasons for this must be looked for elsewhere, and these will be alluded to later.

Results.

The results of the experiments are given in Table I. The measured amount of radon collected from B is given in column 2, and the amount collected from A is given in column 5. Column 4 gives the radon in B in curies per cm.^{3} B was at room temperature, which was taken in the calculations uniformly as 17° C. The pressure

TABLE I.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Observed Values.			Calculated Values.							
T. Abs. temp.	Radon in B, 10^{-6} curie.	Volume of B, cm.^{3}	Rn in B, $\frac{10^{-6}\text{ curie}}{\text{cm.}^3}$.	Radon in A, 10^{-6} curie.	Radon condensed in A, 10^{-6} curie.	$p\ 10^{-10}$ atm. Pressure of Rn in B at 290° abs.	$P\ 10^{-10}$ atm. Equilibrium pressure in A at T., $P=p\frac{T}{290}$.	Log P.	$\frac{1}{T}$.	
114·1	11130	31·21	357	5030	1790	2265	1422	— 6·847	0·00877	C
109·4	5630	,,	180·4	3095	1455	1144	705	— 7·152	·00913	C
108·8	7300	31·65	230	7130	1408	1458	894	— 7·049	·00919	Y
108·4	5380	31·21	172·2	3750	2187	1092	668	— 7·175	·00923	C
108·1	4710	,,	151	7520	6150	958	589	— 7·230	·00925	C
107·1	2980	,,	95·5	12500	11532	606	368	— 7·434	·00934	C
107·1	7490	96·2	77·9	2495	1572	494	299	— 7·524	·00934	Y
106·1	3600	31·21	115·3	17810	16662	731	444	— 7·353	·00942	C
105·1	2330	,,	74·6	15480	14802	473	286	— 7·544	·00951	C
104·4	4830	96·2	50·2	1027	432	318	191	— 7·719	·00957	Y
102·6	3175	31·21	101·7	2255	1333	645	384	— 7·416	·00974	C
102·5	3228	31·65	102	2900	1692	647	386	— 7·413	·00975	Y
100·1	1650	31·21	52·8	19762	19283	336	197 5	— 7·704	·01001	C
97·1	1087	,,	34·8	6968	6652	221	127·4	— 7·895	·01029	C
95·1	506	39·27	12·9	4365	4212	81·8	46·8	— 8·330	·01052	Y
92·1	75·5	31·21	2·12	12300	12278	15·4	8·68	— 9·062	·01086	C
91·6	212	,,	6·79	12375·5	12314	43·1	2·43	— 9·614	·01091	C
90·1	188	39·27	4·8	4871	4814	30·4	1·71	— 9·767	·01110	Y
86·3	12·2	31·21	0·391	12587·5	12584	2·48	1·36	— 9·866	·01159	C
86·1	62·0	,,	1·99	12230	12212	12·62	6·88	— 9·162	·01161	C
85·6	65·5	,,	2·10	8725	8706	13·32	7·23	— 9·141	·01165	C
85·1	12·4	,,	0·397	19750	19746	2·52	1·36	— 9·866	·01175	C
84·6	6·35	,,	0·204	4678	4676	1·295	0·70	—10·155	·01182	C
84·1	30·2	39·27	0·77	5059	5050	4·88	2·63	— 9·580	·01189	Y
83·6	11·3	31·21	1·323	21412	21400	8·39	4·52	— 9·345	·01196	C
83·1	8·3	,,	0·266	9130	9128	1·70	0·91	—10·041	·01206	C
80·1	16·73	96·2	0·174	771	769	1·105	0·58	—10·237	·01248	Y
80·1	4·3	31·65	0·136	12220	12218	0·86	0·46	—10·337	·01248	Y
79·6	10·38	39·27	0·265	6128	6125	1·72	0·88	—10·056	·01256	Y
143·1	1820	31·21	58·3	186	None	...	...	...	...	C
117·1	9600	,,	308	2006	,,	...	...			C

produced by the radon in B at 290° absolute can be calculated by using the value for the volume of 1 curie at N.P.T. The mean of the experimental values of Rutherford, Debierne, and Gray & Ramsay ,weighting their mean values equally, is $5{\cdot}97 \times 10^{-4}$ cm.^{3} Using Geiger and Werner's * value for the number of α-particles emitted per second per gram radium, we get the same volume. Consequently, 1 curie per cm.^{3} at 290° absolute produces a pressure of $5{\cdot}97 \times 10^{-4} \times \frac{290}{273} = 6{\cdot}342 \times 10^{-4}$ atmosphere. Column 7 gives the pressure in B at 290 abs. calculated from the amount of radon per cm.^{3} as given in column 4. Now, the pressure in B at 290° absolute was in equilibrium with radon at a different pressure (Knudsen) in A, which was at the low temperature. Knudsen found that at low pressures, when the mean free path of molecules was very large in comparison with the size of the tube, the pressures at places of different temperature were connected by the relation $\frac{p}{\sqrt{T}} = \text{constant}$. Consequently the pressure of the gaseous radon in A can be calculated from $\frac{p}{\sqrt{290}} = \frac{P}{\sqrt{T}}$, where p and P are the pressures in B and A respectively. These values are given in column 8, and are the pressures of gaseous radon in equilibrium with condensed radon at a temperature T. The letters C and Y in the last column refer to the experiments performed at Cambridge and Yale respectively. The total volume of A was 11·86 cm.^{3} and 9·08 cm.^{3} for the C and Y experiments respectively, and the volume immersed in the bath at T temperature was 0·46 cm.^{3} and 0·52 cm.^{3} respectively. Using these data, a calculation can be made giving, at least approximately, the amount of gaseous radon in A, and by subtracting this amount from the amount of radon collected from A, one gets a value giving approximately the amount of radon condensed in A. These quantities are entered in column 6. The results given at the end of the table show according to such calculation that no radon was condensed in those experiments. Plotting the pressure in atmospheres against the absolute temperature, one gets the curve in fig. 2 ; and plotting the common logarithm of the pressure against the reciprocal of the absolute temperature, one gets the distribution of points shown

* Geiger & Werner, *Zs. f. Phys.* xxi. p. 187 (1924).

in fig. 3. The straight line drawn in fig. 3 is the nearest approach to a linear relation of the form $\log P = -a \cdot \frac{1}{T} + K$. In this case $a = 970{\cdot}15$, $K = 1{\cdot}787$. Selecting seven points from the smooth curve in fig. 2, as given in Table II. below, and assuming the form of relation between P and T

Fig. 3.

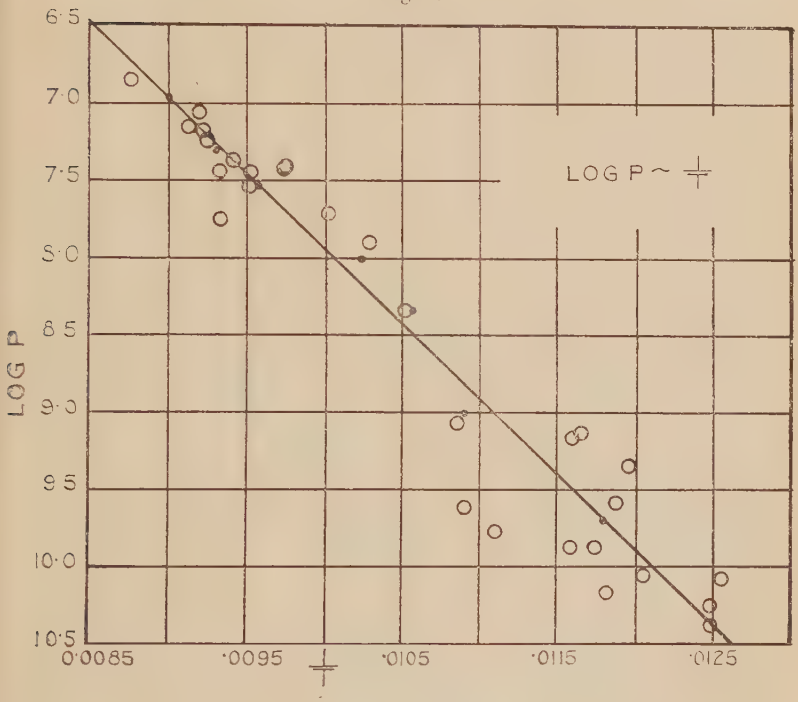


TABLE II.

P.	T.	$\frac{1}{T}$.	$\log_{10}$ P.	
1100×10^{-10} atm.	111·1 abs.	0·00900	3·04139 − 10	−6·9586
500 „	107·4 „	·00931	2·69897 − 10	−7·3010
300 „	104·4 „	·00958	2·47712 − 10	−7·5229
100 „	97·8 „	·01023	2·00000 − 10	−8·0000
45 „	94·6 „	·01057	1·65321 − 10	−8·3468
10 „	91·7 „	01091	1·00000 − 10	−9·0000
2 „	84·7 „	·0118	0·30103 − 10	−9·6990

to be $\log P = -a\frac{1}{T} + b \log T + C$, one gets the following values of a, b and c:—$a = 968{\cdot}479$, $b = 0{\cdot}3021$, $c = 1{\cdot}1579$; and if natural logarithms are used, $a' = 2230{\cdot}0$, $b' = 0{\cdot}3021$, $c' = 2{\cdot}6662$. If the form of the equation is

$$\log P = -a\frac{1}{T} + \frac{5}{2}\log T + C,$$

we get for the constants (common logarithms used)

$$a = -822{\cdot}5 \quad \text{and} \quad c = -4{\cdot}77.$$

The best representation is given by

$$\log P = -968{\cdot}479\,\frac{1}{T} + 0{\cdot}3021 \log T + 1{\cdot}158.$$

Discussion of the Results.

Even though the points do not fall on a smooth curve and are somewhat irregularly spaced, the results give ample evidence that an equilibrium seems to exist between the gaseous state and the condensed state of small quantities of radon. It cannot be said that the condensed state represents solid radon. In fact, from what follows, one must conclude that the condensed state does not form uniformly and in the same way in the various experiments, and that it is probably a monatomic condensation and may be in parts also solid radon. In support of this idea the following deductions may be used. If Gray and Ramsay's results are plotted as $\log P$ against $\frac{1}{T}$, one gets a straight line which is well represented by the equation $\log P = -863\,\frac{1}{T} + 4{\cdot}083$. This equation gives the relation between gaseous radon and liquid radon in equilibrium. If we extrapolate to the temperature of solid radon which Gray and Ramsay give as 202° abs. (or to about 160° abs., which is probably more nearly correct *) and obtain the equilibrium pressure, and do likewise by using the equation representing the relation of radon and "condensed" radon as found in these experiments, we shall find that the extrapolated pressure from Gray and Ramsay's equation will be upwards of 500 times as great as the pressure obtained from the equation representing the results of these experiments. Assuming the permissibility of extrapolation in both cases, the pressures should be

* Paneth & Rabinowitsch, *Ber. d. Deut. Chem. Ges.* lviii. p. 1138 (1925).

the same. It seems justifiable to conclude that in the "condensed" state of the small quantities of radon in these experiments, the work function is greater than it would be if the condensed state represented truly a solid radon obtained by freezing liquid radon, and that probably all or part of the condensed radon is in a less-than-monatomic layer. If the U-tube in which the radon is condensed in liquid air is taken out of its bath and viewed, it is found to be luminous throughout, but shows some specks of greater brightness than the general luminosity. It is therefore possible that some radon may condense into a liquid and freeze at points which might for one reason or another be first cooled to the lowest temperature; and if this is so, and if these points may be different in different experiments, the relative amounts of solid radon and otherwise monatomic condensed radon will be different, and the average work function may be different in different experiments even if the temperature of the bath should be the same. This may explain the somewhat irregularly-spaced points along the curve, although here one may argue that the thermocouple junction, placed as it was on the outside lower end of the U-tube, may not give accurately the temperature of the radon in the tube. In the long time taken during each experiment for the bath to become constant, it would seem that only a slight shift along the temperature axis should result, whereas a varying force function will account for the greater irregularities observed. If these irregularities are due to a slightly wrong temperature reading, they should not be so pronounced as the curve (shown on enlarged scale) for the *low* temperatures shows them to be.

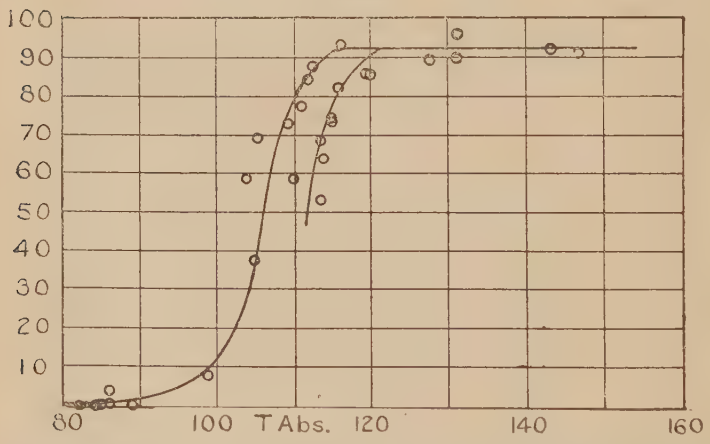
Also, if we assume the pressure from Gray and Ramsay's equation for the freezing temperature of radon, and substitute into the equation obtained from these experiments and solve for T, we shall get a temperature about twice as great as that assumed for the freezing temperature. This is quite in accord* with experiments on the temperature at which monomolecular layers of vapours may be driven off the surface on which they are condensed, the temperature being much above the boiling-point of the substance.

As a further support of the argument that the condensation is very likely not always of one kind, it is desired to refer to some preliminary experiments on the volatilization temperature of small quantities of radon in a glass tube, using the

* Becker, J. A., Phys. Rev. (2) xxviii. p. 341 (1926); but compare also Holst & Clausing, *Physica*, vi. p. 48 (1926).

apparatus of the preceding experiments. In the apparatus exhausted to a low pressure the radon in A was subjected to a definite temperature for at least half an hour. The vessel B was connected to A for half a minute. The radon diffusing into B was then collected in C, and so was also the remainder of the radon in A. The radon collected from B as a fraction of the total amount used is plotted against the temperature in fig. 4. It is desirable in these experiments to make the time of diffusion as short as possible, so as to prevent possible evaporation on account of the reduced pressure, and yet get the major part of the gaseous radon. Experimenting with radon in A at room temperature, it was found that in half a minute over 90 per cent. of the radon was diffused into B, and at low temperatures half a minute

Fig. 4.



was found to be the most suitable time for the diffusion. The radon collected becomes an approximate measure of the gaseous radon in A. A break in the curve should indicate the volatilization or condensation temperature. It will be noted from fig. 4 that for low temperatures the points can be arranged along two curves, one of which may be a variable one depending on the apparatus. The two volatilization temperatures seem to be about 116° and 121° absolute, the sort of values recorded by other investigators for the volatization temperature.

If condensation of small quantities of radon may take place in these two ways—namely, to form at certain points of initial lowest temperature minute droplets of liquid radon, and these later freeze and at other points (the rest of the cooled surface) single atoms become attached to the surface

of the glass,—and if the vapour pressures of these two states are different, it would seem that if a sufficiently long time were allowed, that state which has the greater vapour pressure would change into the other. If the time required to effect this is long, intermediate values of vapour pressure would be measured in the actual experiment.

In connexion with the equation giving the relation between pressure and temperature, it may be of interest to note that the constant $C = 1{\cdot}158$ has a value which does not differ much from $\frac{3}{2}\log 222 - 1{\cdot}622 = 1{\cdot}898$, where 222 is the atomic weight of radon and $-1{\cdot}622$ is the "universal constant" of Edgerton *.

Summary.

1. In summarizing, it can be said that the gaseous radon existing in actual or transient equilibrium with the condensed radon was collected and measured, and from such determinations for various low temperatures it was found that the deduced vapour pressure decreased with the lowering of temperature, and that its value is connected with the temperature by the equation

$$\log P = -968{\cdot}479\frac{1}{T} + 0{\cdot}3021 \log T + 1{\cdot}158.$$

2. The distribution of the points in the pressure-temperature curve shows irregularities far too great to be accounted for by experimental errors. This indicates a possible explanation that the condensation may be partly monatomic on the cooled surface and partly frozen minute droplets of radon. This argument is supported by various deductions and observations.

3. The volatilization temperatures of small quantities of radon condensed in a glass tube seem to be either 116° or 121° absolute.

In conclusion, I desire to thank Professor Sir Ernest Rutherford for the hospitality and continued friendship shown me, and suggesting the work on this interesting problem and for placing at my disposal the necessary equipment. I also wish to express my gratitude to the Memorial Hospital in New York City for their kindness in supplying me with the radon used in the experiments at Yale in checking up and extending the observations made at Cambridge.

Yale University, New Haven.
June 1, 1927.

* Edgerton, A. C., Phil. Mag. (6) xxxix. p. 1 (1920).

CXII. *The Crystallography of some Simple Benzene Derivatives.* By W. A. Caspari, *D.Sc.*, *Ph.D.**

THE investigation of crystals of organic substances of which the structural formulæ (as decided by chemical evidence) are based on the benzene ring has not, so far, brought any certainty as to the configuration of atoms in benzene and its derivatives in the crystal state. The hydrocarbons naphthalene and anthracene have indeed yielded to X-ray examination preliminary results of considerable interest †, and several other benzene and naphthalene derivatives have been studied. Advances in our knowledge of the crystal structure of such derivatives are to be expected either from advances in X-ray technique and interpretation or, as was found practicable in the case of naphthalene and anthracene, from comparisons of the X-ray data for different crystals. It may be well, therefore, to place on record the primary data for as many crystals as possible.

The substances here dealt with contain, chemically speaking, one benzene ring with no other substituent groups than hydroxyl, $-OH$, and the amino-group, $-NH_2$. The only mono-substituted body of this class which is solid at ordinary temperatures is phenol. Owing to its deliquescence and volatility, phenol is difficult of treatment by goniometric or X-ray methods, and only tentative data as to its crystallography have hitherto been published. Of the di-substituted derivatives, however, the three dihydroxybenzenes have been examined both goniometrically ‡ and by X-rays §. Para-phenylene-diamine ‖, ortho-phenylene-diamine ¶, and para-amino-phenol ** have received attention from crystallographers, but no members of these two groups have been subjected to X-ray analysis.

The X-ray examination of the crystals described in the sequel has been carried out mainly by the rotating-crystal method, followed by indexing of the reflexion spots appearing on the photographs. The cell-dimensions, number of molecules in the cell, and space-group have been determined.

* Communicated by the Author.

† W. H. Bragg, Proc. Phys. Soc. Lond. xxxiv. p. 33 (1921).

‡ P. Groth, *Chem. Krystallographie*, iv. pp. 84–87.

§ W. H. Bragg, J. Chem. Soc. cxxi. p. 2766 (1922). W. A. Caspari, *ibid.* 1926, pp. 573, 2944; 1927, p. 1093.

‖ C. Hintze, *Zeits. f. Kryst.* iv. p. 552 (1884).

¶ P. Groth, *ibid.* iv. p. 276.

** W. Keith, *N. Jahrb. f. Min.* vi. p. 196 (1889).

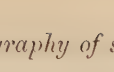
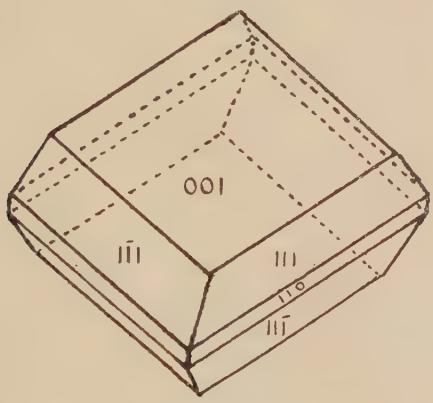
Ortho-phenylene-diamine,  , crystallizes from water, chloroform, or benzene in flat plates of almost rectangular contour. With this crystal, as with many others, the rule was found to hold good that solvents of the water and alcohol type are apt to exaggerate tabular or acicular habit, whilst those of the chloroform and benzene type produce crystals of a more isometric tendency. The crystal is found to be monoclinic-prismatic, $\beta = 121^\circ\ 10'$, principal forms (001), (111), ($11\bar{1}$), and (110), the latter feebly developed (fig. 1). Density, determined in this and the succeeding

Fig. 1.



o-Phenylene-diamine.

cases by flotation in a mixture of chloroform or carbon disulphide with petroleum spirit, 1·205. The X-ray photographs gave the following results :—

Cell-dimensions, $a = 7{\cdot}74$ Å.

„ $b = 7{\cdot}56$ Å.

„ $c = 11{\cdot}76$ Å.

No. of molecules in cell, $n = 4$ (found, 3·98).

The *c*-axis diagram exhibits very markedly preponderating intensities in even layer-lines ; a layer of molecules very similar to that in (001) is therefore to be expected halfway up the *c* axis of the cell. Reflexions from 40 planes in all were identified in the photographs, the strongest being from (001), (110), (112), (120), and (122). No halvings were apparent among the (*hkl*) planes, but in all the (*h*0*l*)

planes noted (ten altogether) h was even. Reflexions from (010) and (020) occur. The crystal must be placed in space-group C_{2h}^4, with the simple lattice Γ_m (*cf.* Astbury and Yardley's Tables, Phil. Trans. 1924, cciv. p. 221).

Meta-phenylene-diamine, , is even more easily oxidizable than the other substances here dealt with, and should be freshly distilled before crystallization. Crystals may be obtained by slow evaporation of chloroform solutions, or by cooling of melted substance to which a little water has been added. They are orthorhombic-bipyramidal, and have the habit of rectangular parallelopipeds showing (100), (010), and (001), rarely also small dome and pyramid faces. Their general tendency is to be tabular along (001) and somewhat elongated along the b axis. Density 1·225. The X-ray data are as follows :—

$$a = 11{\cdot}97 \text{ Å}.$$
$$b = 8{\cdot}14 \text{ Å}.$$
$$c = 23{\cdot}61 \text{ Å}.$$

16 molecules to the cell (found, 15·86).

The photographs are unusually well filled with reflexion spots. The greatest intensity is shown by (014), (024), (114), (124), (120), (200), (210), and (221). In all these diagrams the row-lines are for the most part occupied by spots without a gap up to the farthest layer-line. There are therefore no halvings, and the space-group can only be Q_h^1, with the simple lattice Γ_0. With this lattice, however, there cannot be more than eight asymmetric molecules to the cell. Meta-phenylene-diamine, therefore, would appear to be one of the examples, several of which are now known, of a crystal in which more than one molecule—in this case two—unite to form an asymmetric lattice unit.

Para-phenylene-diamine, , crystallizes from solvents of the acetone and alcohol type in monoclinic-prismatic plates tabular along (001) having the habit described by Hintze (*l. c.*). Petroleum spirit yields excessively thin leaflets of rhomboidal contour. From chloroform, compact all-round crystals are obtained in which several faces of the $h0l$ zone are well developed. Density 1·245. For the X-ray rotation photographs, Hintze's axes and β-angle

were taken and confirmed by the photographs themselves. The results are as follows :—

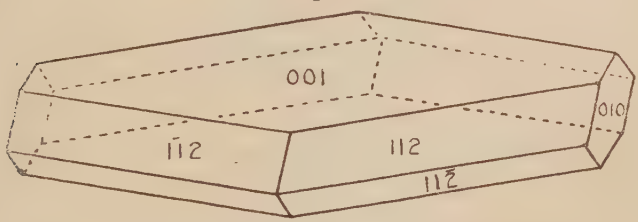
$a = 8{\cdot}29$ A.
$b = 5{\cdot}93$ Å.
$c = 24{\cdot}92$ A.
$\beta = 112° 58'$ (Hintze).

8 molecules to the cell (found, 7·85).

The crystal reacts exceptionally well to the X-rays, and 57 planes were identified on the photographs, the strongest reflexions being from (004), (011), (110), (111), (11$\bar{1}$), (10$\bar{4}$), (200), and (201). No (*hkl*) or (*h*0*l*) halvings could be traced, but (010) and its higher orders do not appear. The space-group therefore appears to be C_{2h}^2, simple lattice Γ_m. In the absence of (*hkl*) halvings, however, four asymmetric molecules suffice for the symmetry of the cell, whereas this cell, as we have seen, contains the substance of eight molecules. It must be concluded that here again the lattice-unit consists of two molecules so coupled as to form an asymmetric whole.

Ortho-amino-phenol, , forms flat plates of rectangular contour which are pseudo-tetragonal, but are actually found to be orthorhombic-bipyramidal (fig. ·2),

Fig. 2.



o-Amino-phenol.

showing mainly (001) and (112), occasionally also (010) Density 1·328. The X-ray data are :—

$a = 7{\cdot}26$ Å.
$b = 7{\cdot}71$ Å.
$c = 19{\cdot}51$ Å.

8 molecules to the cell (found, 8·07).

The strongest reflexions (among 39 planes identified) are

4 0 2

from (002), (120), (112), (211), (212), (221), and (222). There are no halvings in the (*hkl*) series. The base is represented by the second, fourth, and eighth orders; (020) and the whole series (021) to (026) occurs; the remaining planes parallel to axes are (200), (120), (220), (204), and (304). The inference is that (*hk*0) and (0*kl*) are halved when *k* is odd, and that (*h*0*l*) is halved when *l* is odd. The crystal may therefore be assigned to the space-group Q_h^{15}, simple lattice Γ_0.

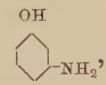
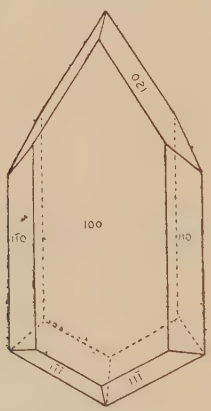
Meta-amino-phenol,  , crystallizes from the various solvents with much the same habit, in characteristic ortho-rhombic-pyramidal crystals of pronounced hemimorphism

Fig. 3.



m-Amino-phenol.

(fig. 3), tabular along (100). Density 1·195. The X-ray data are :—

$$a = 6{\cdot}14 \text{ Å}.$$
$$b = 11{\cdot}10 \text{ Å}.$$
$$c = 8{\cdot}38 \text{ Å}.$$

4 molecules to the cell (found, 4·09).

Among the 26 planes identified, (002) and (111) show the most intense reflexions. There are no (*hkl*) halvings. The reflexions from planes parallel to axes, of which 11 occur, indicate that (0*kl*) is not halved, but that (*h*0*l*) is halved when *l* is odd. The crystal may therefore be placed in space-group C_{2v}^4, simple lattice Γ_0.

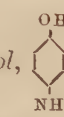
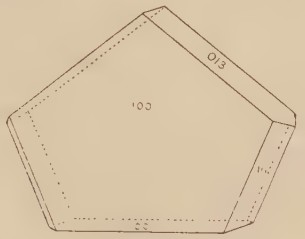
Para-amino-phenol,  , was assigned by Keith (*l. c.*) to the orthorhombic-bipyramidal class, with faces (100), (010), (110), and (011) developed. On looking more closely into the crystallization of this substance, it is found that there are at least two polymorphs, which we may call α and β. Of these, the more stable, or α-modification, appears to be the crystal examined by Keith, but it is distinctly hemimorphic and should be placed in the pyramidal class.

Fig. 4.



p-Amino-phenol.

Crystals may be obtained from solutions in alcohols, water, or ethyl acetate. From the latter solvents there is a tendency towards elongation along *c*, with a well-marked basal pedion; from alcohols, crystals elongated along *a* are deposited. In both cases (100), (013), and (111), are the principal other forms present, with occasional developments of (110) and (113). The density is 1·290, and the X-ray data are as follows:—

$$a = 8{\cdot}25\ \text{Å}.$$
$$b = 5{\cdot}32\ \text{Å}.$$
$$c = 13{\cdot}06\ \text{Å}.$$

4 molecules in the cell (found, 4·11).

The strongest reflexions, out of 27 noted, are from (110), (111), (201), and (211), and there are no (*hkl*) halvings. Fourteen planes parallel to axes are represented, such that (*h*0*l*) would appear to be halved when *h* is odd, and (0*kl*) when *l* is odd. The space-group C_{2v}^5, simple lattice Γ_0, is therefore indicated.

β-Para-amino-phenol.—When acetone is used as the crystallizing solvent, a second modification separates out in acicular crystals which, since on keeping they soon turn into

opaque pseudomorphs consisting of α-para-amino-phenol, are clearly a less stable form under ordinary conditions. The crystals are simple rectangular parallelopipeds bounded by the three pinacoids and elongated along *c*. Here and there small developments of (110) and (111) were noticed. Although the symmetry is very nearly tetragonal, Laue photographs showed it to be definitely orthorhombic and to be planar—that is, the crystal is either orthorhombic-bipyramidal or orthorhombic-pyramidal ; the latter class is not excluded, even though no hemimorphism was revealed by microscopic examination. The X-ray results are :—

$$a = 12{\cdot}07\ \text{Å}.$$
$$b = 11{\cdot}85\ \text{Å}.$$
$$c = 5{\cdot}82\ \text{Å}.$$

6 molecules to the cell (found, 6·03).

The photographs are richer in spots than those of the α-modification, 43 planes being identified. On the *c* photograph the reflexions may be expected to be largely double spots, owing to the pseudo-tetragonal symmetry. The main difference in aspect between the *a* and *b* photographs lies in the presence of (210) and (410) in the former, and a strong (200) reflexion together with the absence of (120) and (140) in the latter. Intense reflexions are especially shown by (011), (101), (210), (220), and (211). No halvings of any sort could be traced, and the space-group Q_h^1, simple lattice Γ_0, is therefore indicated. Eight asymmetric molecules, however, is the smallest number required for a cell of this class. Since there are actually six molecules in the cell, it follows that the lattice-unit comprises the substance of three molecules, the cell containing only two such units. The major part of the crystal symmetry resides, therefore, in the lattice-units themselves, each of which must be symmetrical about two planes if the crystal is holohedral, or about one plane if it is hemimorphic. For a group of three molecules to possess this degree of symmetry, each individual molecule must possess it also. Now, it is unlikely that the molecule should be symmetrical about two planes, for the highest molecular symmetry hitherto met with in an aromatic compound is a centre. Probably, then, the crystal is really hemimorphic and comes under space-group C_{2v}^1. The crystal is evidently of an unusual sort ; but tri-molecular lattice-units are not unknown, and it is remarkable that such units occur in the fully-hydroxylated analogue of *p*-amino-phenol, namely quinol.

Summarizing the data now at hand for the present group of benzene derivatives, with the inclusion of those previously examined, we have :—

	a.	*b*.	*c*.	β.	*n*.
Catechol	17·46	10·74	5·48	94° 15′	8
Resorcinol	9·56	10·25	5·64	—	4
Quinol α	22·07	—	5·62	—	18
do. β	16·25	—	5·53	—	9
do. γ	13·24	5·20	8·11	107°	4
o-Amino-phenol	7·28	7·71	19·51	—	8
m-Amino-phenol	6·14	11·10	8·38	—	4
p-Amino-phenol	8·25	5·32	13·06	—	4
do. β ...	12·07	11·85	5·82	—	6
o-Phenylene-diamine	7·74	7·56	11·76	121° 10	4
m-Phenylene-diamine	11·97	8·14	23·61	—	16
p-Phenylene-diamine	8·29	5·93	24·92	112° 58′	8

It will be seen that, pending closer insight into the several structures, there are no such strikingly comparable data as in the case of naphthalene and anthracene. Taking the ortho-, meta-, and para-isomers of any one derivative, the dihydroxy-benzenes at least show one marked feature in common, in that one cell-dimension is about 5·5 Å. long in all three. Moreover, the intensities of the X-ray reflexions indicate that the planes corresponding to this spacing are in no case interleaved ; hence this side of the cell would appear to be fully occupied by the spatial extent of one molecule. If we assume atoms to be actually grouped in molecules according to the structural chemical formulæ, and apply the known approximate atomic domains of carbon and hydrogen, this spacing would agree with the breadth of the hexagonal benzene ring. The thickness of a benzene ring can hardly exceed 3 Å., whilst the length of a molecule over any of the substituent groups must be not far from 7 Å.

On comparing different derivatives having substituents in the same position the similarity between *o*-amino-phenol and *o*-phenylene-diamine, as regards the *a* and *b* axes, attracts notice. On the basis of atomic domains, the spaces occupied by OH and NH_2 cannot differ greatly from one another, and the longest molecular dimension of any of the above ortho-compounds would correspond to this cell-side. Catechol, indeed, is wholly different, but its cell is a face-centred one ; besides, it is always possible that there may be hitherto undetected polymorphs.

On comparing *para*-compounds, we find a remarkable connexion between the cell-dimensions if the cell of *p*-phenylene-diamine be cut in half along the *c* axis. The several cells may be written down thus :—

γ-Quinol	*a*, 13·24	*b*, 5·20	*c*, 8·11
α-*p*-Amino-phenol	*c*, 13·06	*b*, 5·32	*a*, 8·25
p-Phenylene-diamine	$\frac{1}{2}c$, 12·46	*b*, 5·93	*a*, 8·29

The regular progression in these figures suggests that the molecules are arranged somewhat similarly in the three crystals, and that at least one of the cell-dimensions represents the span of a molecule. Since the overall length of any of the above molecules would work out, from atomic domains, at rather over 8 Å., the cell-sides in the last column may be so occupied. Some justification for treating the *p*-phenylene-diamine cell as a double one is to be found in the subdivision of the *c* axis of this crystal, mentioned above; also in the circumstance that the lattice-units are bimolecular.

For the present, any identification of a particular spacing with the "chemical" molecule can be no more than speculative. Certain arithmetical relations common to the cell-dimensions of all the simple benzene derivatives hitherto studied do, however, emerge. The cell-dimension 5·5 Å. and its integral multiples, as also $1{\cdot}5 \times 5{\cdot}5 = 8{\cdot}34$ Å. and its multiples, are observed to occur over and over again, as shown by the subjoined table :—

	Multiples of 5·5.			Multiples of 8·34.		
	a.	*b*.	*c*.	*a*.	*b*.	*c*.
Catechol	3·16	1·95	1·00	2·09	—	—
Resorcinol	—	1·87	1·02	—	—	—
Quinol α	4·00	—	1·02	—	—	—
do. β	2·96	—	1·01	1·95	—	—
do. γ	—	0·95	—	—	—	0·97
o-Amino-phenol	—	—	—	—	—	—
m-Amino-phenol	—	2·00	—	—	—	1·00
p-Amino-phenol	—	0·97	—	—	—	0·99
o-Phenylene-diamine ...	—	—	2·14	—	—	—
m-Phenylene-diamine ...	—	—	4·29	—	0·98	—
p-Phenylene-diamine ...	—	1·07	—	0·99	—	3·09
do. β ...	—	—	2·14	—	—	—
Benzene	—	—	1·05	—	—	—
Benzoic Acid	0·99	—	3·96	—	—	—

The figures represent the quotient of the various cell-dimensions by 5·5 and 8·34. Out of 80 cell-dimensions in all, 27 are found to be nearly integral multiples of one or the other length. The data for benzene and benzoic acid are taken from earlier X-ray work. Whatever the significance of these lengths may be, their occurrence seems too persistent to be merely accidental.

In conclusion, the author desires to express his acknowledgements to Sir Wm. Bragg, F.R.S., for the interest he has taken in this work, and to Dr. A. Müller for some valuable suggestions.

Davy-Faraday Laboratory,
The Royal Institution.

CXIII. *A Theory of Porous Flow.* *By* Earl E. Libman, *Physics Department, University of Illinois* *.

WHENEVER a material containing a fluid dries, the fluid is conducted from the interior to the surface. It is the purpose of this paper to develop mathematically the laws governing this flow.

Let

f_n = mass of fluid flowing in unit time through unit area normal to the direction n.

v = mass of fluid per unit mass of dry material. We will call this the "moisture density."

ρ = density of moist material.

σ = density of dry material.

τ = density of fluid.

w = mass of dry material in volume V of moist material.

E = mass of fluid evaporating in unit time from unit area of surface.

β = coefficient of compressibility of moist material.

Consider any closed surface lying wholly inside the given material. The rate at which fluid flows into the surface through the area dS is

$$-(\lambda f_x + \mu f_y + \nu f_z)\, d\mathrm{S},$$

where $\lambda\,\mu\,\nu$ are the direction cosines of the outwardly

* Communicated by the Author.

directed normal to the surface. Hence,

$$-\iint(\lambda f_x+\mu f_y+\nu f_z)\,dS$$

is the rate of gain in fluid by the volume within the closed surface. If this volume is V, then

$$-\frac{1}{w}\iint(\lambda f_x+\mu f_y+\nu f_z)\,dS$$

is the rate of gain in fluid per unit mass of dry material. But the rate of increase in fluid per unit mass of dry material is the rate of increase in $\bar{v}$, where $\bar{v}$ is the average value of v within the closed surface. Hence,

$$\frac{\partial\bar{v}}{\partial t}=-\frac{1}{w}\iint(\lambda f_x+\mu f_y+\nu f_z)\,dS$$

$$=-\frac{1}{w}\iiint\left(\frac{\partial f_x}{\partial x}+\frac{\partial f_y}{\partial y}+\frac{\partial f_z}{\partial z}\right)dx\,dy\,dz\ . \quad (1)$$

by Green's Theorem, and this holds for any closed surface inside the material. Applying it to an element of volume surrounding the point P(x, y, z), we have

$$\frac{\partial v}{\partial t}=-\frac{dx\,dy\,dz}{w}\left(\frac{\partial f_x}{\partial x}+\frac{\partial f_y}{\partial y}+\frac{\partial f_z}{\partial z}\right). \quad . \quad . \quad (2)$$

Now, the mass of fluid in the volume V is $w\bar{v}$ and the total mass of volume V is $w\bar{v}+w$. But the total mass of volume V is also ρV. Hence

$$w=\frac{\rho}{1+\bar{v}}\mathrm{V}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

When $\mathrm{V}=dx\,dy\,dz$, then $\bar{v}=v$, and (2) becomes

$$\frac{\partial v}{\partial t}=-\frac{1+v}{\rho}\left(\frac{\partial f_x}{\partial x}+\frac{\partial f_y}{\partial y}+\frac{\partial f_z}{\partial z}\right)\text{ in the interior.} \quad (4)$$

On the bounding surface of the material consider an element of area dS. Upon dS, and within the solid, erect a small cylinder normal to the surface of height ϵ. Let p be the perimeter of dS and let n be the normal to the surface at dS. Then the rate of flow of fluid into the cylinder through the inside face is $f_n dS$. The rate of flow into the cylinder through the curved face is $fp\epsilon$, where f is the average rate of flow per unit area into the curved face. The rate of evaporation from dS is E dS. Hence the rate of gain in fluid by the cylinder is $f_n dS+fp\epsilon-\mathrm{E}\,dS$. Now, the volume

of the cylinder is $\epsilon\, dS$, and by Eq. (3) the mass of dry material in this volume is $\frac{\rho}{1+v}\epsilon\, dS$. Hence the rate of gain in fluid by the cylinder per unit mass of dry material is

$$(f_n dS - fp\epsilon - E dS)/\left(\frac{\rho\epsilon}{1+\bar{v}}\right) = \frac{\partial v}{\partial t}.$$

Thus we get

$$(f_n - E)\, dS + fp\epsilon = \frac{\rho\epsilon}{1+\bar{v}}\frac{\partial \bar{v}}{\partial t},$$

and taking the limit as $\epsilon \to 0$ gives

$$f_n - E = 0. \quad \text{Boundary condition} \quad . \quad . \quad . \quad (5)$$

The flow of fluid in a porous material may be considered as due to three causes, first, the flow due to capillarity, second, the flow due to pressure gradient caused by shrinkage of the material, and third, the flow due to gravity.

If we consider a non-shrinking porous body, such as unglazed porcelain, and observe the flow in a horizontal direction so that gravity does not affect the results, we find that the flow takes place from points of higher to points of lower moisture content. There is little doubt that the rate of flow at any point is proportional to the moisture density gradient at that point, and we will make this assumption

$$f_{n_{\text{cap.}}} = -K\frac{\partial r}{\partial n}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It is well known (see Schlichter, Nineteenth Report of U.S. Geological Survey, 1897–98) that the rate of flow of a fluid through a porous material due to pressure is given by

$$f_{n_{\text{press.}}} = -k\frac{\partial p}{\partial n}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Finally, the flow due to gravity, which is always in the direction $-z$, is

$$f_{n_{\text{gravity}}} = -kg\tau\cos(zn) = -kg\tau\frac{\partial z}{\partial n}. \quad . \quad . \quad . \quad (8)$$

Consider now a small element of volume at P(xyz) containing the mass δw of dry material. The volume of this element is, by Eq. (3) $\frac{1+v}{\rho}\delta w$, and, dividing this by the mass of dry material (namely, δw) we have for the volume

per unit mass of dry material at the point P(x, y, z)

$$\mathrm{V} = \frac{1+v}{\rho}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Then

$$\frac{d\mathrm{V}}{dv} = \frac{d}{dv}\left(\frac{1+v}{\rho}\right) \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\frac{dp}{dv} = \frac{dp}{d\mathrm{V}}\frac{d\mathrm{V}}{dv} = \frac{d}{dv}\left(\frac{1+v}{\rho}\right) \cdot \frac{dp}{d\mathrm{V}}. \quad . \quad . \quad (11)$$

But

$$\beta = -\frac{1}{\mathrm{V}}\frac{d\mathrm{V}}{dp} \text{ by definition.}$$

Hence

$$\frac{dp}{dv} = -\frac{d}{dv}\left(\frac{1+v}{\rho}\right) \cdot \frac{1}{\mathrm{V}\beta} = -\frac{1}{\beta}\left[\frac{d}{dv}\left(\frac{1+v}{\rho}\right)\right] \Big/ \left(\frac{1+v}{\rho}\right)$$

$$= -\frac{1}{\beta}\frac{d}{dv}\left(\log\frac{1+v}{\rho}\right), \quad . \quad (12)$$

$$\frac{\partial p}{\partial n} = \frac{dp}{dv}\frac{\partial v}{\partial n} = -\frac{1}{\beta}\frac{d}{dv}\left(\log\frac{1+v}{\rho}\right) \cdot \frac{\partial v}{\partial n}, \quad . \quad . \quad . \quad . \quad (13)$$

and substituting Eq. (13) in Eq. (7), we have, adding Eqs. (6), (7), and (8),

$$f_n = -\left[\mathrm{K} - \frac{k}{\beta}\frac{d}{dv}\left(\log\frac{1+v}{\rho}\right)\right] \cdot \frac{\partial v}{\partial n} - kg\tau\frac{\partial z}{\partial n}, \quad (14)$$

or, putting

$$\frac{d\phi}{dv} = \mathrm{K} - \frac{k}{\beta}\frac{d}{dv}\left(\log\frac{1+v}{\rho}\right) \quad . \quad . \quad . \quad . \quad (15)$$

$$f_n = -\frac{\partial\phi}{\partial n} - kg\tau\frac{\partial z}{\partial n}. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Note that ϕ, as a function of v only, is, for a given fluid, a property of the material. We will call it the "flow function."

From Eq. (16) we get

$$f_x = -\frac{\partial\phi}{\partial x}, \; f_y = -\frac{\partial\phi}{\partial y}, \; f_z = -\frac{\partial\phi}{\partial z} - kg\tau, \quad . \quad (17)$$

and putting this into Eq. (4) we get

$$\frac{\rho}{1+v}\frac{\partial v}{\partial t} = \frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2}, \quad . \quad . \quad . \quad (18)$$

while from Eq. (15)

$$\frac{\partial \phi}{\partial n} + \mathrm{E} + kg\tau \frac{\partial z}{\partial n} = 0. \quad \text{Boundary condition.} \quad (19)$$

Special Case of no Shrinkage.

In the special case where there is no shrinkage an element of volume δV does not change in volume. Hence the mass of dry material in δV is $\sigma \delta V$ and the mass of fluid is $\sigma v \delta V$. The total mass is then $\sigma \delta V + \sigma v \delta V$, and dividing this by the volume δV gives the density

$$\rho = \sigma(1 + v). \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Thus $\frac{1+v}{\rho} = \frac{1}{\sigma}$, a constant, and Eq. (15) becomes

$$\frac{d\phi}{dv} = \mathrm{K}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Now, when there is no shrinkage, there is no change in the capillary structure of the material, and so K, which depends only on the structure, is constant. We have then

$$\phi = \mathrm{K}v + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

and Eq. (18) becomes

$$\frac{\partial v}{\partial t} = \frac{\mathrm{K}}{\sigma}\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial z^2}\right), \quad . \quad . \quad . \quad (23)$$

while Eq. (19) gives

$$\mathrm{K}\frac{\partial v}{\partial n} + \mathrm{E} + kg\tau \frac{\partial z}{\partial n} = 0. \quad \text{Boundary condition.} \quad (24)$$

Note that Eq. (23) is the equation of heat flow. *The flow of fluid within a non-shrinking porous body is analogous to the flow of heat.* For almost any problem in flow for the case of a non-shrinkable porous body we can find its analogue in heat flow solved in one of the numerous treatises on the subject and the transition is easily made.

Determination of the "Flow Function" ϕ.

In order to use the Eqs. (18) and (19) it is necessary to know the flow function ϕ as a function of v. We proceed to consider a method of determining ϕ experimentally.

Consider a bar of the material in question of length L. Let us prevent evaporation from the surface by painting the surface with wax or otherwise. Let one end of the bar be immersed in fluid and the other end kept in a constant

atmosphere. After a time equilibrium will be established and at any point the moisture density v will not vary with time. Then Eq. (18) becomes

$$\frac{\partial^2 \phi}{\partial x^2} = \overset{\circ}{1} \text{ when } 0 < x < L, \quad . \quad . \quad . \quad . \quad (25)$$

and Eq. (19) gives

$$\frac{\partial \phi}{\partial x} + E = 0 \text{ when } x = L. \quad . \quad . \quad . \quad . \quad (26)$$

These give

$$\phi = Ex + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Now, let us slice up our bar into slices perpendicular to its length and, by weighing each slice, drying, and weighing again, get v as a function of x, or x as a function of v. Putting this in Eq. (27) we have ϕ as a function of v if we know E as a function of v. The constant is arbitrary, since only the derivatives of ϕ enter into our equations. Knowing ϕ as a function of v, equation (18) must be solved for v as a function of t, x, y, z, with Eq. (19) as the boundary condition.

Determination of ρ *and* E.

If a piece of the material under investigation is taken and its dimensions and weight determined at intervals of time, while it is drying under the same atmospheric conditions as used in the experiment just discussed, we have data whereby to determine its density ρ and rate of evaporation per unit area E* as functions of v.

The problem of drying is an important one in many industries, especially where, as in the pottery and brick industries, it is desirable to dry as quickly as possible and yet not cause cracking due to the shrinkage strains set up in the process. It is evident that the function ϕ is the governing entity in the procedure, and the writer hopes that data on the values of ϕ for different materials will be investigated. The problem of the distribution of stress due to drying is now under consideration.

* For clays E takes a very simple form, being constant and equal to the rate of evaporation from a free water surface. (Results of work soon to be published by Professor H. K. Hursh, Ceramics Department, University of Illinois.)

CXIV. *The Transparency of Turbid Media.*

By Ludwik Silberstein.—(Communication No. 318.) *

IN a recent paper on the transparency of a developed photographic plate as observed under various conditions †, it was assumed that the total light scattered by each particle (grain) is sent forward, *i. e.* in the direction of and under acute angles with the incident light beam. It is well known that if the scattering particle, supposed to be spherical, is very small compared with the wave-length, then, according to Rayleigh's elementary theory and Mie's developed form of the electromagnetic theory ‡, one-half of the scattered light is sent forward and one-half backward §, the distribution of the intensity being perfectly symmetrical with respect to the plane passing through the particle and normal to the incident beam. For particles, however, whose size is comparable with the wave-length, there is a tendency of the scattered light to concentrate in the forward direction. This tendency, derived theoretically but tested also experimentally ‖, is for gold particles, for instance, already very pronounced at a diameter of $160\,\mu\mu$ (with $\lambda=550$), while for somewhat larger particles ($180\,\mu\mu$) practically the whole scattered light is sent forwards, as a glance on Mie's figures (*l. c.* p. 429) will show. These and similar examples computed by Shoulejkin ¶, who pushed the ratio of particle size to wave-length up to the value of two or three units, have suggested the adoption of the said assumption in the case of the black silver grains of photographic emulsions, these grains being in general of the order of the wave-length of visible light. (Commonly, their diameters range from a few tenths to several whole microns.) The assumption of a unilateral spreading of the scattered light recommended itself also by the obvious simplicity of its consequences. Moreover, the object of that paper was only to correlate with each other the two kinds of photographic "density" (diffuse and specular) without studying each of them in detail as a function of the size and the number of particles, and for this purpose the assumption

* Communicated by the Author. From the Research Laboratory of the Eastman Kodak Company.

† L. Silberstein and C. Tuttle: "The Relation between the Specular and Diffuse Photographic Densities," J. O. S. A. & R. S. I. xiv. (1927).

‡ G. Mie, *Ann. der Physik*, xxv. pp. 377–455 (1908).

§ Unless the particle is a perfect conductor, when almost the whole light is scattered backwards. *Cf.* Mie, *l. c.* p. 430.

‖ As, *e. g.*, by R. Gans, *Ann. der Physik*, lxxvi. p. 29 (1925).

¶ W. Shoulejkin, Phil. Mag. xlvii. p. 307 (1924).

turned out to be accurate enough. It has therefore been adopted in that connexion, although implying the rather uncertain extrapolation from Mie's spherical metallic particles to the generally larger, shapeless, and sponge-like silver grains of the photographic plate.

In the present paper the problem of light transmission through turbid media will be treated without this special simplifying hypothesis. It will be assumed that of the light scattered (or re-scattered) by each particle a certain fraction (ζ) is sent forward and the remainder backward, the numerical value of this fraction being left free. The equations corresponding to this general case are somewhat more complicated, but can be solved without trouble.

Consider a plane-parallel layer of absorbing and scattering particles which will be supposed to be all equal. Let I_0 be the intensity of the incident light collimated normally to the layer at its front surface ($x=0$) and I the intensity of the directly transmitted light which has penetrated to any depth x. The total energy scattered (per unit time) by a particle which is struck by this light can again be written AI, where A, the scattering coefficient, will be a function of wave-length, etc. Of this energy let the fraction

$$\zeta AI$$

be sent forward and the remainder $(1-\zeta)AI$ backward (along rays, that is, which make with the incident beam angles 0 to $\pi/2$ and $\pi/2$ to π respectively). Let κI be the energy absorbed by a particle, N the number of particles per unit volume, and $dn=Ndx$. Then, in the first place, we will have for the directly transmitted light

$$\frac{dI}{dn}=-(\kappa+A)I, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which is independent of the partition of the scattered light.

Next, if, at any depth x, S be the total flux of scattered light energy directed forward and S' that directed backward, a first contribution to dS/dn will be ζAI and $(1-\zeta)AI$ will be one to $-dS'/dn$, the role of x being for the retrograde flux S' replaced by $-x$. Further, of the scattered radiation S the amount κS will be absorbed and the amount AS will be re-scattered per particle; of the latter, however, the fraction ζAS is again sent forward so that only $(1-\zeta)AS$ is lost to the S-flux. Finally, the amount of S' re-scattered is AS', and of this $\zeta AS'$ is sent in the negative and $(1-\zeta)AS'$ in the positive direction of the x-axis. Thus the

equation for S becomes

$$\frac{dS}{dn}=\zeta AI-\kappa S-(1-\zeta)AS+(1-\zeta)AS',$$

and similarly, the equation for S',

$$-\frac{dS'}{dn}=(1-\zeta)AI-\kappa S'-(1-\zeta)AS'+(1-\zeta)AS,$$

or, collecting the terms

$$\frac{dS}{dn}=\zeta AI-\alpha S+(1-\zeta)AS', \quad . \quad . \quad . \quad . \quad (2)$$

$$-\frac{dS}{dn}=(1-\zeta)AI-\alpha S'+(1-\zeta)AS, \quad . \quad . \quad (3)$$

where $\alpha=\kappa+(1-\zeta)A$.

(1), (2), (3) are the required differential equations for the three light fluxes*. In addition to these we have the boundary conditions, viz. at the front surface ($x=0$) of the layer, $I=I_0=1$, say, and

$$S=0, \text{ for } n=0, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and at the back surface,

$$S'=0, \text{ for } n=\bar{n}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where n is the total number of particles per unit area of the layer. (For $\zeta=1$ this system of equations reduces at once to our previous formulæ, *loc. cit.*)

By (1),

$$I=e^{-pn},$$

where $p=\kappa+A$. Thus the directly transmitted light would still obey Beer's simple law.

To satisfy the equations (2) and (3), put

$$S=re^{-pn}+ae^{\beta n}+be^{-\beta' n},$$

$$S'=r'e^{-pn}+a'e^{\beta n}+b'e^{-\beta' n},$$

where r, r', etc. are constants to be determined. Substituting

* An explicit consideration of distinct light fluxes directed back and forth has already been introduced in A. Schuster's treatment of the problem of an incandescent "foggy atmosphere," 'Astrophysical Journal,' xxi. p. 1 (1905). Schuster limits himself, however, to the special case of equal distribution (*i. e.* $\xi=\frac{1}{2}$), which would suit only very small particles. Moreover, he has no term representing the collimated radiation but, in accordance with the nature of his subject, considers only the scattered fluxes in either sense. This leads to two equations only, which (apart from the emission terms) differ somewhat from (2) and (3).

into (2), (3), and comparing the coefficients of the three exponentials, we find, first of all

$$r+\frac{1-\zeta}{\zeta}r'=-1,$$

$$r-\frac{\alpha+p}{(1-\zeta)A}r'=-1,$$

so that $r'=0$ and $r=-1$.

Next,

$$\frac{a'}{a}=\frac{\alpha+\beta}{(1-\zeta)A}=\frac{(1-\zeta)A}{\alpha-\beta}=\lambda, \text{ say,}$$

and

$$\frac{b'}{b}=\frac{\alpha-\beta'}{(1-\zeta)A}=\frac{(1-\zeta)A}{\alpha+\beta'}=\mu, \text{ say.}$$

The first pair of these equations gives

$$\beta=\pm\sqrt{\alpha^2-(1-\zeta)^2A^2},$$

and the second pair gives exactly the same expression for β'. Thus, either $\beta'=\beta$ or $\beta'=-\beta$. But in the latter case we would have $\lambda=\mu$, and, by the boundary condition (5), $a+b=0$. This, however, would clash with the condition (4) which calls for $a+b=1$. We are left, therefore, with

$$\beta'=\beta=\sqrt{\alpha^2-(1-\zeta)^2A^2}=\sqrt{\kappa^2+2(1-\zeta)\kappa A}. \quad . \quad (6)$$

(Taking the negative square-root we would only interchange the roles of a and b.)

The two fluxes now become

$$S=ae^{\beta n}+be^{-\beta n}-e^{-pn}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$S'=\lambda ae^{\beta n}+\mu be^{-\beta n}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where

$$\lambda=\frac{\alpha+\beta}{(1-\zeta)A}, \quad \mu=\frac{\alpha-\beta}{(1-\zeta)A}. \quad . \quad . \quad . \quad (9)$$

The coefficients a, b will be determined by the boundary conditions (4) and (5), *i. e.*

$$a+b=1, \quad \lambda ae^{\beta\bar{n}}+\mu be^{\beta\bar{n}}=0,$$

whence, writing henceforth n instead of $\bar{n}$,

$$a=\frac{\mu e^{-\beta n}}{\mu e^{-\beta n}-\lambda e^{\beta n}}, \quad b=\frac{-\lambda e^{\beta n}}{\mu e^{-\beta n}-\lambda e^{\beta n}}. \quad . \quad . \quad (10)$$

Thus, by (7),

$$S=\frac{\lambda-\mu}{\lambda e^{\beta n}-\mu e^{-\beta n}}-e^{-pn},$$

where λ, μ are as in (9).

Ultimately, therefore, the emergent scattered light flux,

proceeding forward, is

$$S=\frac{2\beta}{(\alpha+\beta)e^{\beta n}-(\alpha-\beta)e^{-\beta n}}-e^{-(\kappa+A)n}, \quad . \quad . \quad (11)$$

where

$$\alpha=(1-\zeta)A+\kappa, \quad \beta=\sqrt{\kappa^2+2(1-\zeta)A\kappa},$$

and the intensity of the directly transmitted, collimated light

$$I=e^{-(\kappa+A)n}.$$

Thus the total transmitted light flux $S+I$ or (since $I_0=1$) the *total transparency* of the layer, as recorded, say, by means of an integrating sphere, will be

$$S+I=\frac{2\beta}{(\alpha+\beta)e^{\beta n}-(\alpha-\beta)e^{-\beta n}}, \quad . \quad . \quad . \quad (12)$$

which contains the original three constants only through their two combinations, α and β *. It is this total transparency which is unambiguously observable, while it would be hard to isolate I from the superposition of some unknown fraction of S. In photographic nomenclature $-\log(S+I)$ would be the "diffuse density." Notice that in general only I itself satisfies Beer's law, while S and $S+I$ do not obey this law. (In the particular case $\zeta=1$ we have $\alpha=\kappa=\beta$, so that $S=e^{-\kappa n}-e^{-pn}$, as in the first paper on this subject. In this case both I and $I+S$ obey Beer's law.) For small values of βn the total transparency (12) reduces to $\frac{1}{1+\alpha n}$, and for large βn to $\frac{2\beta}{\alpha+\beta}e^{-\beta n}$.

It may still be interesting to determine the total scattered light S' thrown *backward* and emerging at the front surface ($x=0$) of the layer. This will be obtained by putting in (8) $n=0$. Thus

$$S'=\lambda a+\mu b,$$

* This differs, even for $\zeta=\frac{1}{2}$, from Schuster's result (*loc. cit.*) as regards the coefficients. In fact, Schuster's formula for the total emergent radiation R reduces, in absence of emission, to

$$R=4c/[(1+c)^2e^{\beta n}-(1-c)^2e^{-\beta n}],$$

where, in our symbols $c=\sqrt{\frac{\kappa}{\kappa+A}}$, while $\beta=\sqrt{\kappa(\kappa+A)}$, identical with our β for $\zeta=\frac{1}{2}$. The difference in the structure of the coefficients is due to the fact that no collimated light (flux I) has been taken into account. The dependence on n, however, or equivalently on the thickness of the layer (*cf. infra*) is essentially the same. Schuster's type of formula has also been obtained by an entirely different reasoning by Channon, Renwick, and Storr, Proc. Roy. Soc. xciv. p. 222 (1918).

i. e., by (10) and (9),

$$S' = (1-\zeta)A\,\frac{e^{\beta n}-e^{-\beta n}}{(\alpha+\beta)e^{\beta n}-(\alpha-\beta)e^{-\beta n}}, \quad . \quad . \quad (13)$$

or, compared with the total forward flux,

$$\frac{S'}{S+I} = \frac{(1-\zeta)A}{2\beta}(e^{\beta n}-e^{-\beta n}). \quad . \quad . \quad . \quad (14)$$

For indefinitely increasing n the emerging backward flux (13) tends to

$$S' = \frac{(1-\zeta)A}{\alpha+\beta},$$

a finite value, as might have been expected.

In all these formulæ n or $\int N dx$ is the number of particles over unit area, whether their distribution in depth is uniform or not. If it is uniform (N=const.), the same formulæ hold good when n stands for the thickness of the layer, only that κ and A are then the original constants multiplied by N, *i. e.* the absorption and the scattering coefficients, not per particle but per unit volume.

Rochester, N.Y.,
May 12, 1927.

CXV. *Some Comments on the Classical Theories of the Absorption and Refraction of X-Rays.* *By* F. K. Richtmyer *.

Abstract.

The assumptions usually made in the classical approach to the problem of the absorption of X-rays are summarized, and a relation is derived similar to that previously deduced by Kronig (J. O. S. A. and R. S. I. vol. xii. p. 554) between the index of refraction and the atomic absorption coefficient. It is shown that the relation is experimentally verified in so far as order of magnitude is concerned, but that an exact verification cannot be made because of the absence of data on absorption at long wave-lengths. However, it is doubtful whether a real verification of the formula is to be expected, since, by limiting the solution of the differential equation of motion of the electron oscillators to forced vibrations, expressions for scattering rather than for (fluorescent) absorption should result. It is pointed that all writers except Thomson introduce the λ^3 law of absorption as an experimental datum.

* Communicated by the Author. The author acknowledges with thanks his indebtedness to the Heckscher Research Council of Cornell University.

A different method of approach to a possible relation between absorption and refraction of X-rays is suggested by considering the equations of classical optics, which have led to an approximately correct expression for index of refraction of X-rays. It is shown that these equations, too, lead to expressions for scattering. The main part of X-ray absorption, namely fluorescent absorption—a photoelectric process on the basis of our modern quantum picture—is therefore, as might be expected, unexplained by these strictly classical methods.

THEORIES of the absorption of X-rays have been developed on strictly classical grounds by J. J. Thomson *, Houstoun †, A. H. Compton ‡, and, recently, Bothe §. These theories assume :—

(1) That in the absorbing material there are (harmonic) electron oscillators of several kinds (K, L, M, ...), and that the natural frequencies of the oscillators of each kind extend from the frequency ν of the corresponding absorption limit to infinity.

(2) That the electric moment f of any one oscillator of natural frequency ν_0, when acted on by the periodic electric vector $\mathrm{E}=\mathrm{E}_0 \sin 2\pi\nu t$ of a light-wave of frequency ν, can be represented by the equation

$$\ddot{f}+k\dot{f}+(2\pi\nu_0)^2 f=\frac{e^2}{m}\mathrm{E}_0 \sin 2\pi\nu t, \quad . \quad . \quad (1)$$

where e and m are the charge and mass respectively of the electrons.

(3) That the term $k\dot{f}$, which ordinarily represents damping due to friction, is identified with the damping due to the radiation from the accelerated electron. If the rate $d\mathrm{W}/dt$ of radiation from an accelerated electron is given by the classical expression

$$\frac{d\mathrm{W}}{dt}=\frac{2}{3}\frac{e^2\ddot{x}^2}{c^3},$$

it follows that k in equation (1) is given by

$$k=\frac{2}{3}\frac{e^2}{mc^3}(2\pi\nu)^2.$$

* J. J. Thomson, 'Conduction of Electricity through Gases,' 2nd edition, p. 321.

† Houstoun, Proc. Roy. Soc. Edinburgh, xl. p. 34 (1919); Phil. Mag. (7th ser.) ii. p. 512 (Sept. 1926).

‡ A. H. Compton, National Res. Council, Bull. xx. p. 37 (1922).

§ Bothe, *Zeits. f. Physik*, xl. p. 653 (Jan. 1927).

(4) *That transient effects have disappeared,* and that the electron is executing forced vibrations of frequency ν.

Now, the "friction" term, *if we admit assumption* 4, determines the rate at which energy is being extracted from the incident beam. The intensity of the incident beam is proportional to E_0^2. Using these relations, and making reasonable approximations in the solution of equation (1), the following relation may be derived:

$$\int_{\nu_i}^{\infty} \tau_{i\nu} d\nu = \frac{\pi e^2}{mc} n_i, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $\tau_{i\nu}$ is the absorption coefficient, at frequency ν, of the atom due to all its oscillator, n_i, of kind i. Houstoun* has used a relation of this kind to determine the number of K electrons per atom, obtaining the mean value for some 13 elements of 1·03 electrons per atom.

Equation (2) may be summed up for all the different kinds of oscillator in the atom by writing

$$\sum_i \int_{\nu_i}^{\infty} \tau_{i\nu} d\nu = \frac{\pi e^2}{mc} n, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where n $(=\Sigma n_i)$ is the total number of electrons per atom.

Numerous investigations † of the refraction of X-rays have shown that the classical theories of refraction may be extended to the X-ray region, and that the index of refraction $\mathbf{n}$ is given to an approximation adequate for experimental purposes by

$$1-\mathbf{n} = \delta = \frac{\mathrm{N}ne^2}{2\pi m \nu_r^2}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where N is the number of atoms per unit volume and ν_r the frequency for which $\mathbf{n}$ is determined. If we multiply both sides of the equation (3) by $c\mathrm{N}(2\pi^2\nu_r^2)$, we have, using equation (4),

$$\frac{c\mathrm{N}}{2\pi^2\nu_r^2} \sum_i \int_{\nu i}^{\infty} \tau_{i\nu} d\nu = \delta. \quad . \quad . \quad . \quad . \quad (5)$$

This relation between index of refraction and absorption has been derived by Kronig ‡, using a slightly different procedure.

A rough check of equation (5) is, at least theoretically, possible. The value of δ for platinum, at $\lambda = 0{\cdot}3$ Å., is about

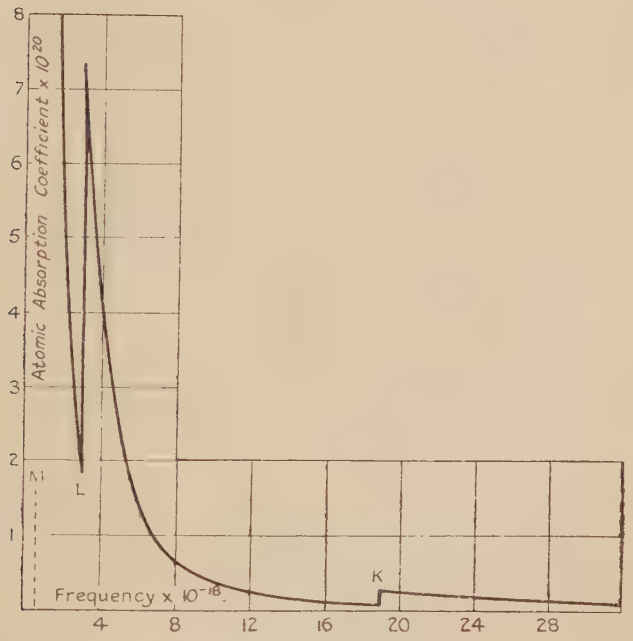
* *Loc. cit.* (Phil. Mag.).

† See A. H. Compton, 'X-Rays and Electrons,' p. 205.

‡ J. O. S. A. and R. S. I. vol. xii. p. 554 (June 1926).

$2 . 10^{-6}$, as given by equation (4). The term $\Sigma_i \int_{\nu_i}^{\infty} \tau_{i\nu} d\nu$ is simply the area, call it S, between the coordinate axes and a curve plotted between the frequency and the *observed* values of (total) atomic absorption coefficient τ_ν. Such a curve is plotted to scale in fig. 1, from data compiled by Compton*. Because of our comparative ignorance of the numerical value of absorption coefficients for X-rays longer than about 2 Å., one can determine only *the order of magnitude* of S, and

Fig. 1.



not its actual value. But knowing that absorption coefficients in the region of long X-rays are very great, we may guess that S might be somewhere in the neighbourhood of 1·2. (Abscissæ are vibrations per second; ordinates are *atomic* absorption coefficients.) This gives a value for δ for Pt, as computed from equation (5) for $\lambda = 0{\cdot}3$ Å., of about $1{\cdot}2 . 10^{-6}$, considerably lower than the value given by equation (4), but at least of the right order of magnitude.

However, the relation between τ and δ is not quite so intimate as might be judged from equation (5) taken by

* 'X-Rays and Electrons,' p. 185.

itself. Equation (5) is, in fact, derived from equating the two values of n, given independently by equations (3) and (4) respectively. And equation (2), from which equation (3) is deduced, gives, as mentioned above, only one instead of two K electrons per atom. A similar result is pointed out by Kronig *. Hence equation (5) may be expected to yield too low a value for δ.

Indeed, the approximate numerical verification of equation (5) may even be fortuitous. For the limitation of the solution of equation (1) to the forced vibrations, after transients have disappeared, should lead to a determination of the *scattering* coefficient, rather than the *absorption* coefficient, which latter is given experimentally by the approximately correct relation

$$\tau_a = CZ^4\lambda^3,$$

where τ_a is the observed atomic absorption coefficient for wave-length λ, Z is the atomic number of the absorber, and C is a constant which depends on the spectral region. With the exception of J. J. Thomson's, the classical theories *do not lead to an independent theoretical justification for the law*

$$\tau_a \propto \lambda^3.$$

Rather this law is introduced *as an experimental datum* †, and an equation of the type

$$\tau_a = 2\pi \frac{e^2}{mc^2}\left(\sum_i \frac{n_i}{\lambda_i^2}\right)\lambda^3$$

results. But Thomson, by a procedure which amounts to taking transient effects into account, deduced theoretically the λ^3 law, although Thomson's complete formula,

$$\tau_a = \frac{\pi^3}{3}\frac{e^2}{mc^2}\left(\sum_i \frac{n_i}{\lambda_i^2}\right)\lambda^3,$$

gives values for τ_a about five times too large.

That the classical theories, when restricted to the forced vibration of the electrons, lead to a determination of scattering coefficients, is easily seen by considering the companion equation to the one from which equation (4) is derived. The well-known equations showing the relation, for frequency ν, between the index of refraction $\mathfrak{n}$ and the

* *Loc. cit.* p. 555.

† See, for example, Bothe (*loc cit.*).

extinction coefficient κ, are*:

$$\mathbf{n}^2(1-\kappa) = 1 + \frac{4\pi m(\nu_0^2-\nu^2)\mathrm{N}ne^2}{4\pi^2m^2(\nu_0^2-\nu^2)^2+p^2\nu^2}, \quad . \quad . \quad . \quad (6)$$

$$\mathbf{n}^2\kappa = \frac{\mathrm{N}ne^2p\nu}{4\pi^2m^2(\nu_0^2-\nu^2)^2+p^2\nu^2}. \quad . \quad . \quad . \quad . \quad (7)$$

Here, as before, N is the number of atoms per unit volume, n the number of "mobile" electrons per atom, ν_0 is the natural frequency of the electron oscillators, and p is the constant of the so-called friction term $p\dot{x}$ in the ordinary equation of motion of the electron. If, as before, the damping be due to radiation, the numerical value of p is given by

$$p = \frac{8\pi^2}{3}\frac{e^2}{c^3}\nu^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The relation between the extinction coefficient κ and the absorption coefficient μ is given by

$$\kappa = \mu\frac{\lambda}{4\pi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

μ being expressed in cm.$^{-1}$ †.

Now, in the X-ray region $\kappa \leqslant 1$, and $\mathbf{n}$ differs from unity by only a small quantity. Hence, assuming that damping is small (*i. e.*, that $p^2\nu^2 \leqslant 4\pi^2m^2(\nu_0^2-\nu^2)^2$), equation (6) at once reduces to equation (4), which in turn agrees with experiment. It might therefore be expected that a similar treatment of equation (7) would lead to a value of the absorption coefficient μ. Making these approximations, and using the values of p and κ from equations (8) and (9), one obtains from equation (7)

$$\mu = \frac{8\pi}{3}\cdot\frac{\mathrm{N}ne^4}{m^2c^3}\cdot\frac{\nu^4}{(\nu_0^2-\nu^2)^2}, \quad . \quad . \quad . \quad . \quad (10)$$

which, for $\nu \geqslant \nu_0$, is identical with the Thomson expression for *scattering*. Therefore κ is related to the scattering coefficient σ rather than to the absorption coefficient μ.

Further, without making the approximation that $p^2\nu^2 \leqslant 4\pi^2m^2(\nu_0^2-\nu^2)^2$, by combining equations (6) and (7) one obtains, using equations (8) and (9) as before,

$$\frac{\mu}{\rho} = \frac{16\pi^2}{3}\cdot\frac{e^2}{mc^2}\cdot\frac{\lambda_0^2}{\lambda^2(\lambda^2-\lambda_0^2)}\delta, \quad . \quad . \quad . \quad . \quad (11)$$

where μ/ρ should be the *mass* absorption coefficient for

* See, for example, Campbell's 'Modern Electrical Theory,' 2nd edition, p. 51.

† That is, μ is given by the equation $\mathrm{I}=\mathrm{I}_0e^{-\mu x}$, which gives the intensity I of a beam of radiation of incident intensity I_0 after passing through a slab of the material x cm. thick.

X-rays of wave-length λ, ρ being the density of the absorber and λ_0 the characteristic wave-length emitted by its oscillators. Using this equation to compute the mass absorption coefficient for silver at $\lambda = 1{\cdot}297$ Å., for which $\delta = 20 \cdot 16^{-6}$ as determined experimentally by Compton, one obtains

$$\left(\frac{\mu}{\rho}\right)_{Ag} = 2{\cdot}3 ;$$

whereas μ/ρ for silver, at this wave-length, is approximately 150 *. Clearly, the value 2·3 corresponds more closely to the scattering coefficient. We have, however, no data on scattering with which to make even an approximate check of equations (10) and (11) at various wave-lengths.

These classical methods of approach to the problem of X-rays lead therefore to expressions for scattering, but leave untouched the main part of the absorption process—namely, the part which is proportional to the cube of the wave-length and which, in the modern quantum picture of the phenomenon, is associated with the expulsion of electrons. This failure is in entire harmony with the failure of classical theory to explain even qualitatively he essential facts of the photoelectric effect. It may, nowever, be a significant circumstance that Thomson, by considering the *potential* energy stored in the oscillator as a result of the passage of a light-wave, does succeed in deriving the λ^3 law, and thereby in giving a picture of the mechanism by which characteristic (*i. e.* fluorescent) radiation is emitted by the absorber.

Cornell University.
May 8, 1927.

CXVI. *The Crystal Structure of* Cu_3, Sn, *and* Cu_3Sb.

By W. Morris Jones, *M.A., M.Sc., and* Prof. E. J. Evans, *D.Sc., University College, Swansea* †.

IT is generally considered that a definite intermetallic compound is formed on the solidification of two liquid metals: (i.) if the solid so formed is of the same composition throughout; (ii.) if the solid contains the metal in approximately simple proportions; and (iii.) if the colour, density, hardness, electrical conductivity and other physical properties of the solid are in sharp contrast with those of the

* Computed from the writer's experimental equation (Phys. Rev. xxvii. p. 5, Jan. 1926). Allen (Phys. Rev. xxviii. p. 907) gives a slightly lower value.

† Communicated by the Authors.

component metals, or with those which might be expected if one metal was in a state of solid solution in the other.

Condition (ii.) has led to fixing a chemical formula for the compound with the inevitable association of a chemical molecule and the scheme of valency. In a large number of intermetallic compounds, however, the formulæ do not agree with the usual valencies assigned to the atoms. The X-ray study of the crystal structure of inorganic solids shows that in most crystals examined, the usually assumed chemical molecule cannot be distinguished, and that the unit of the solid state would appear to be a cell, the repetition of which in space makes up a crystal.

In the extension of the X-ray method to the investigation of the crystal structure of alloys, the nature of solid solution has, so far, been the main object of study. The results of these investigations show that when the end members of a continuous series of solid solutions have the same crystal structure, a unique and perfectly regular lattice is formed, the dimensions of the lattice gradually changing from those of the one to those of the other, as the atoms of one metal replace those of the other on the lattice. If the atoms of two metals are not structurally equivalent, two different structures co-exist over a range of composition, the initial and final structures being those of the two metals.

The crystal structure of very few intermetallic compounds has, so far, been examined *, though the number of such compounds is very large. A study of their crystal structure would, therefore, seem well worth while, especially as the evidence for the formation of a definite compound is not always as conclusive as seems desirable. We have, therefore, examined the crystal structure of a number of intermetallic compounds by the X-ray powder method, and the analyses of the photographs for two of the compounds, Cu_3Sn and Cu_3Sb, are given below.

The alloys were very carefully prepared at the Metallurgical Laboratory, under the direction of Professor C. A. Edwards, and their composition afterwards checked by chemical analysis.

X-ray Apparatus †.

The powder method of X-ray crystal analysis is well known, so the apparatus used in the present investigation need only be briefly described.

* Owen and Preston, Phil. Mag. ii. p. 1266 (1926); iv. p. 133 (1927).

† We are indebted to the Department of Scientific and Industrial Research for defraying the cost of part of the equipment.

The target of the X-ray tube was of copper and water cooled, whilst the cathode was a hot tungsten filament. A low vacuum was maintained by two mercury vapour pumps coupled up in series and working continuously. The voltage across the tube was kept at about 30,000 volts., as suitable for bringing out the characteristic radiation of copper with sufficient intensity. Under these conditions the milliamperes passing through the tube varied from 5 to 6, and the tube could be run continuously, the source of high potential being a high tension transformer.

The camera for taking the photographs was about 10 cm. in diameter, the powder being painted on a hair or fine wire and mounted at the centre. The film, placed round the circumference, was backed by an intensifying screen. Allowing for the thickness of the film and screen, the diameter of the camera was 9·96 cm., and this value was taken in the calculations.

A water-cooled aluminium window, within about 2 cm. of the target, enabled a strong beam of X-rays to issue from the tube. The camera could be brought up close to the window, with the powder about 7 cm. from the target. Good photographs were obtained with exposures ranging from $1\frac{1}{2}$ to 3 hours.

The camera was calibrated by taking a photograph of copper powder, measuring up the film, and seeing how the position of the lines of the pattern agreed with the calculated values from the known structure of copper. The correction for various distances from the centre of the film could then be ascertained. Some photographs were taken with powdered copper and the powdered alloy mixed together. The calibration of these films was, therefore, made from the copper lines on them. The films were measured by means of a travelling microscope, and lines on both sides of the centre were read. The readings agreed to within 1 per cent., and the calibration of the films, by means of the standard copper lattice, brought agreement within about 0·25 per cent.

These corrected readings were then reduced to glancing angles of reflexion, and the plane spacings calculated according to Bragg's law.

In order not to reduce the intensity of the X-ray beam, a nickel filter for the K_β radiation was not employed. Though the lines due to K_α and K_β appeared on the films, no confusion was caused, and a little familiarity with the films enabled the lines to be easily sifted out.

The results of the analysis of the photographs are given in the Tables below.

1. *The Crystal Structure of* Cu_3Sn.

Table I.—Cu_3Sn.

Copper K_α radiation. The value of λ_{K_α} is taken as 1·540 Å. Diameter of camera 9·96 cm. Close-packed hexagonal structure. Axial ratio 1·572.

Indices of form.	Distance of lines from centre in mm.			θ in degrees.		$\frac{\lambda}{2\sin\theta}$	Theoretical spacing $\frac{c}{1{\cdot}572}$.	Observed intensity.	Calculated intensity.
	Film (1).	Film (2).	Mean.						
$10\bar{1}0$	32·76	32·84	32·80	18°	52′	2·381 Å.	·381 Å.	·20	·23
0002	36·28	36·38	36·33	20	54	2·159	2·161	·40	·24
1011	37·74	37·83	37·78	21	44	2·080	2·084	1·00	1·00
1012	50·08	50·00	50·04	28	47	1·599	1·599	·27	·18
$11\bar{2}0$	59·07	59·17	59·12	34	1	1·377	1·375	·30	·26
$10\bar{1}3$	67·22	67·20	67·21	38	40	1·233	1·235	·40	·29
2020	69·82	70·02	69·92	40	13	1·192	$1{\cdot}190_5$	·05	·015
$11\bar{2}2$	72·16	72·34	72·25	41	34	1·160	1·159	·30	·34
$20\bar{2}1$	73·40	73·42	73·41	42	14	1·146	1·147	·17	·24
0004	79·16	79·27	79·21	45	34	1·079	$1{\cdot}080_5$	·07	·05
2022	82·94	82·99	82·96	47	43	1·041	1·042	·07	·065
1014	89·88	89·90	89·89	51	42	·981	·983	·08	·058
2023	99·46	99·38	99·42	57	12	·916	·916	·20	·15
2130	102·43	102·48	102·46	58	56	·899	·899	·07	·046
$21\bar{3}1$	106·27	106·28	106·27	61	8	·879	·880	·20	·26
$11\bar{2}4$	113·81	113·76	113·79	65	28	$·846_5$	·848	·24	·16
2132	—	118·83	118·83	68	21	$·828_5$	·830	·12	·08

Column 6 gives the plane spacings deduced from the observations, while column 7 gives the spacings calculated for a close-packed hexagonal structure with axial ratio 1·572.

The observed lines are thus accounted for by a close-packed hexagonal structure * for Cu_3Sn, with axial ratio 1·572.

The dimensions of the unit hexagonal prism deduced from the data are a_0 (base) $=2{\cdot}749$ Å., and c_0 (height) $=4{\cdot}322$ Å., corresponding to an axial ratio $c=1{\cdot}572$.

* Bain, Chem. Met. Eng. xxviii. p. 69, states that Cu_3Sn is close-packed hexagonal in type (like zinc), but gives no further information or any diffraction data.

It is clear from considerations of volume that with the alloy Cu_3Sn, in which the atoms are also as 3 : 1, it is impossible to associate a whole molecule with a cell of the above dimensions. If V is the volume of the cell, M the mass of the chemical molecule, ρ the density of the alloy, then the number of molecules associated with the cell is given by :

$$n=\frac{\rho V}{M}, \text{ where } V=\frac{\sqrt{3}}{2}a_0{}^3c.$$

The density ρ of the alloy was determined by a standard method and yielded the value 8·998 for Cu_3Sn. This result is rather interesting, for the density of copper is 8·93 and that of tin is 7·29, and thus a marked contraction takes place on the formation of this alloy. This phenomenon, however, cannot alone be taken as evidence of the formation of an intermetallic compound, as the same phenomenon also occurs with solid solutions, but in the case of Cu_3Sn the density is greater than that of either component.

Returning to the above equation, and putting in the values of V, ρ, and M, we get $n=0{\cdot}495$, which means that with a cell of the above dimensions half a chemical molecule of Cu_3Sn is associated with it. Assuming the alloy to be a definite compound, such a cell repeated along the three co-ordinate axes would not make up a crystal of the substance, and this cell must, therefore, be a sub-unit of some larger crystal unit. Much time and trouble have been taken in searching the films and giving long exposures to discover additional faint lines which would give evidence of this. With exposures of eight hours and 6 milliamperes through the tube, and after a close search of the films, it could not be said with any degree of certainty that such additional lines were present. The number of atoms of copper and tin in the alloy is in the ratio of 3 : 1, whilst the squares of the atomic numbers of copper and tin are in the ratio of 1 : 3. This may account for the absence of some faint lines, taking the scattering effect of an atom as proportional to the square of its atomic number. In the well-known case of KCl, owing to the approximate equality of the atomic numbers of K and Cl, the diffraction data give a sub-unit of the true unit, and, for this compound, it is by comparison with the data for NaCl that the unit deduced is shown to be one-eighth of the true unit cell. We have prepared the compound Cu_3P, where the ratio of atoms is as 3 : 1, and of atomic numbers squared as 4 : 1. Consequently, if

the structure is hexagonal close packing, additional information might be obtained from powder photographs. A few films of this compound have been taken and additional lines can be seen on them, but as the films have not yet been analysed, nothing definite can be said as to the structure. A later paper will give an account of the study of these films.

If we assume all the atoms in the compound Cu_3Sn to be identical, or, better, if we assume a distribution of copper and tin atoms, as would be the case if the alloy was a solid solution, then M in the equation $n=\frac{\rho V}{M}$ should be taken as one-fourth of the mass of a Cu_3Sn molecule. If this is done, $n=2$, showing that two *mean* atoms are associated with the crystal unit. The relative intensities to be expected can be calculated on this basis and compared with the observed intensities of the lines on the photographs.

The intensities may be calculated from the formula * :

$$I \propto j \,.\, d_{hkl}^{2\cdot35} \,.\, (A^2+B^2),$$

where $$A=\Sigma\, N \cos 2\pi(hx+ky+lz)$$

and $$B=\Sigma\, N \sin 2\pi(hx+ky+lz),$$

j being the number of co-operating planes, and N atomic number, and the summation is to be taken over every atom contained in the crystal unit.

Placing a *mean* atom at points (000) and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ in the cell, the other possible positions for the two atoms being eliminated owing to the absence of such simple reflexions as (0001) and $(11\bar{2}1)$, and substituting the values of x, y, z, in the formula, the expression takes the form

$$I \propto j \,.\, d_{hkl}^{2\cdot35} \,.\, N_m^2[(1+\cos 2\pi\{\tfrac{1}{3}h+\tfrac{2}{3}k+\tfrac{1}{2}l\})^2 + (\sin 2\pi\{\tfrac{1}{3}h+\tfrac{2}{3}k+\tfrac{1}{2}l\})^2],$$

where N_m is the atomic number of the *mean* atom.

The relative intensities calculated in this way are entered in Table I. column 9, and the observed intensities are given in column 8. The agreement between the observed and calculated intensities is good, and the relative intensities are the same as those obtained with a pure metal possessing a close-packed hexagonal structure. The cell is depicted in the figure.

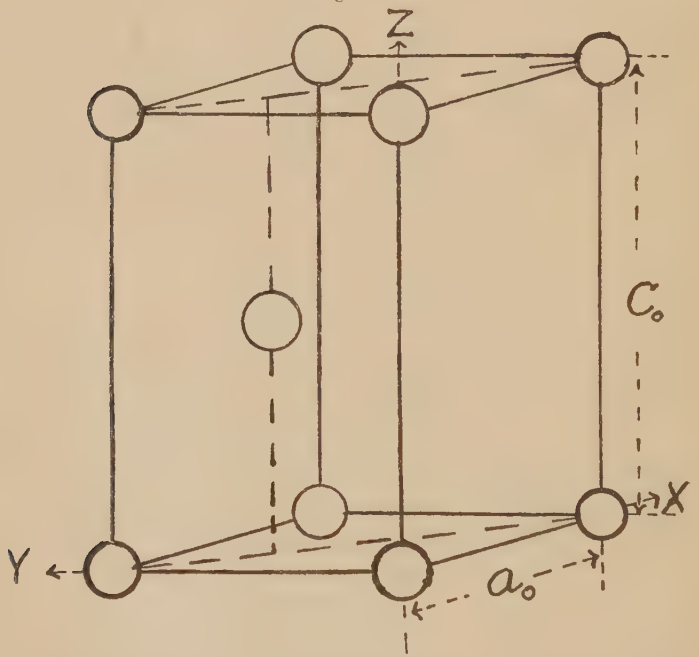
* Wyckoff, 'The Structure of Crystals,' p. 201.

In this cell the distance of closest approach of two atoms is that between atoms at (000) and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$. This distance is equal to

$$a_0\sqrt{\frac{1}{3}+\frac{1}{4}\frac{{c_0}^2}{{a_0}^2}}=2{\cdot}68\ \text{Å}.$$

The nearest distance between atoms in pure tin is 2·80 Å., and in pure copper, 2·54 Å. *, so that the sum of the atomic radii of tin and copper is 2·67 Å. This agrees closely with 2·68 Å. obtained above for the shortest interatomic distance in the structure.

Fig. 1.



The information derived from the photographs is that which would be obtained if all the atoms of the alloy were identical, and the substance crystallized on an hexagonal lattice of the close-packed type. Lines which would enable a larger cell to be deduced are absent. This may be due either to the number of atoms of copper and tin being as 3 : 1, and their atomic numbers squared as 1 : 3, or, perhaps, to the compound Cu_3Sn not being a true compound but a solid solution.

* Bragg, 'X-rays and Crystal Structure,' p. 163.

2. *The Crystal Structure of* Cu_3Sb.

The photographs obtained with Cu_3Sb were exactly similar in pattern and in intensity of the lines to those of Cu_3Sn, but the distances of the lines from the centre of the films were slightly less.

The results of the analysis of these photographs are given in Table II.

TABLE II.—Cu_3Sb.

Copper K_α radiation. The value of λ_{K_α} is taken at 1·540 Å. Diameter of camera 9·96 cm. Close-packed hexagonal structure, axial ratio 1·572.

Indices of form.	Distance of lines from centre in mm.			θ in degrees.	$\frac{\lambda}{2\sin\theta}$.	Calculated spacings.	Observed intensity.	Calculated intensity.
	Film (1).	Film (2).	Mean.					
$10\bar{1}0$	32·50	32·41	32·46	18° 40′	2·406 Å.	2·406 Å.	·20	·23
0002	35·94	35·85	35·89	20 39	2·183	2·183	·40	·24
$10\bar{1}1$	37·54	37·50	37·52	21 35	2·093	2·104	1·00	1·00
$10\bar{1}2$	49·52	49·46	49·49	28 28	1·615	1·615	·27	·18
$11\bar{2}0$	58·76	58·57	58·66	33 45	1·386	1·389	·30	·26
$10\bar{1}3$	66·66	66·66	66·66	38 21	1·241	1·248	·40	·29
$20\bar{2}0$	69·62	69·47	69·55	40 1	1·198	1·203	·05	·045
1122	71·70	71·77	71·74	41 15	1·168	1·173	·30	·34
$20\bar{2}1$	72·87	72·84	72·86	41 55	1·153	1·159	·17	·24
0004	78·21	78·27	78·24	45 1	1·089	1·092	·07	·05
$20\bar{2}2$	82·67	82·68	82·68	47 35	1·043	1·052	·07	·065
$10\bar{1}4$	88·66	89·47	*89·07	51 14	·988	·988	·08	·058
$20\bar{2}3$	98·49	98·34	98·42	56 37	·922	·932	·20	·15
$21\bar{3}0$	101·91	101·83	101·87	58 36	·902	·909	·07	·046
2131	105·50	105·30	105·40	60 38	·884	·890	·20	·26
$11\bar{2}4$	112·49	112·17	112·23	64 37	·852	·858	·24	·16
$21\bar{3}2$	117·74	—	117·74	67 44	·832	·839	·12	·08
$10\bar{1}5$	122·79	—	122·79	70 29	·817	·819	·12	·074

The dimensions of the unit hexagonal prism calculated from the diffraction data are :—

a_0 (base) = 2·777 Å. and c_0 (height) = 4·367 Å.,

corresponding to an axial ratio

$$c_0 : a_0 = 1{\cdot}572.$$

This cell is 3 per cent. larger in volume than the Cu_3Sn cell because of the larger antimony atom.

A determination of the density of the alloy gave the value 8·636. The density of antimony is 6·62, of copper 8·93, and, therefore, the density of the alloy is greater than 8·35 a value based on the proportion of antimony and copper present. A contraction takes place on the formation of the alloy, but the alloy is less dense than Cu_3Sn (8·998), though the atomic weight of antimony (120) is slightly greater than that of tin (119).

Taking the value 8·656 as the density of Cu_3Sb, we get $n=0·49$, so that half a molecule of Cu_3Sb is associated with the cell. If we assume a *mean* atom of mass one-fourth of the mass of the Cu_3Sb molecule as with Cu_3Sn, then $n=2$, and two such atoms would be associated with the cell. Placing such atoms at (000) and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$, the relative intensities of the lines on the photographs can then be calculated in the same way as for Cu_3Sn. The observed and calculated intensities are entered in Table II. columns 8 and 9. These are the same as those entered in Table I., since the atomic numbers of antimony and tin are 51 and 50 respectively, and the unit cells are exactly similar with the same axial ratio.

The distance of closest approach of atoms in antimony is 2·87 Å *, and in pure copper 2·54 Å. The shortest interatomic distance for two atoms in the cell is 2·71 Å., which is almost exactly the sum, 2·705 Å., of the atomic radii of antimony and copper.

As copper itself is face centred cubic with a unit containing four atoms, it would appear that the substitution of one of these atoms by the much larger tin or antimony atom distorts the face centred cubic close-packing, with the result that the aggregate of atoms adjusts itself into the other close-packed arrangement—hexagonal close-packing.

As in the case of Cu_3Sn, the data for Cu_3Sb obtained in these experiments are the same as for a pure metal, such as zinc or magnesium, crystallizing on a close-packed hexagonal lattice containing one kind of atom.

Summary.

The crystal structures of Cu_3Sn and Cu_3Sb have been examined by the X-ray powder method.

Both compounds have close-packed hexagonal structures with axial ratio 1·572 in each case.

* Bragg, 'X-ray and Crystal Structure,' p. 173.

The diffraction pattern and the relative intensities of the lines are the same as obtained with a pure metal possessing a close-packed hexagonal structure. The absence of lines which would give a larger cell may be due to either :—

(i.) that the diffraction effect of an atom is proportional to the square of its atomic number, and that in the above alloys the squares of the atomic numbers of copper and tin or antimony are as 1 : 3, whilst the ratio of the number of the respective atoms in the alloys is as 3 : 1 ; or perhaps

(ii.) that the alloys may not be true compounds but solid solutions.

The dimensions of the hexagonal unit for Cu_3Sn deduced from the diffraction data are $a_0 = 2{\cdot}749$ Å., $c_0 = 4{\cdot}322$ Å.

The shortest interatomic distance for the Cu_3Sn structure is 2·68 Å., agreeing closely with 2·67 Å., the sum of the atomic radii of copper and tin.

The dimensions of the hexagonal unit of Cu_3Sb are $a_0 = 2{\cdot}777$ Å., $c_0 = 4{\cdot}367$ Å.

The shortest interatomic distance for the structure is 2·71 Å. in almost exact agreement with 2·705 Å., the sum of the atomic radii of copper and antimony.

The Cu_3Sb cell is 3 per cent. larger in volume than that of Cu_3Sn, owing to the larger antimony atom.

Both cells are similar to that for a pure metal, such as zinc or magnesium, having a close-packed hexagonal crystal structure.

Powder photographs are being taken of the crystal structure of Cu_3P, where the ratio of the atomic numbers squared is as 4 : 1, and the ratio of the number of atoms as 3 : 1.

If Cu_3Sn and Cu_3Sb are true compounds, then further diffraction data from experiments with single crystals will doubtless be necessary before the distribution of atoms on the lattices and the space group can be determined.

In conclusion, we are grateful to Professor C. A. Edwards for his kindness in supplying us with the alloys and for the special interest he has taken in this research, and also to Professor W. L. Bragg for helpful criticism.

CXVII. *The Hall Effect in Aluminium Crystals in relation to Crystal Size and Orientation.*

By PHYLLIS JONES, *M.Sc.* (*Research Student, University College of Swansea*) *.

INTRODUCTION.

WHEN a metal plate carrying an electric current is placed in a magnetic field, so that the lines of force are normal to the plane of the plate and to the direction of flow of the electric current, a transverse galvanomagnetic potential difference is set up between the edges of the plate. This interesting result was discovered by Hall † in 1879, and from the time of its discovery much work has been done in an attempt to arrive at a satisfactory explanation of the phenomenon.

With this end in view, many experiments have been carried out to try and discover the factors which chiefly influence this effect.

The object of the present paper is to determine whether the Hall effect is in any way influenced by the dimensions and orientation of the crystal aggregates composing the metal. For this purpose experiments were performed with specimens of aluminium which were prepared and presented to the Metallurgical Department of the University College of Swansea by Professor H. C. H. Carpenter, and kindly loaned for the purpose of this research by Professor C. A. Edwards. The specimens were all of the same shape, and of approximately the same dimensions, viz. 23 cm. in length, ·3 cm. in thickness, and 2·5 cm. in width. The size of the crystals varied in such a way that of the eight specimens examined, one contained a single crystal 16 cm. in length, while another contained very small crystals, 183 of which occupied an area of about 1 sq. mm. The remaining six specimens contained crystals of intermediate sizes.

Although aluminium crystallizes in the cubic system, it is still of some interest to determine whether the direction of the primary current with respect to the crystal face has any bearing on the Hall effect ‡.

Again, in the case of the crystalline aggregates, an opportunity is offered for testing whether the conditions at the

* Communicated by Prof. E. J. Evans, D.Sc.

† E. H. Hall, Amer. Journ. Math. vol. ii. p. 287 (1879).

‡ W. L. Webster (Proc. Camb. Phil. Soc. vol. xxiii. part 7, p. 800, July 1927) finds that the Hall coefficient in single crystals of iron is independent of the direction in the crystal, and that the effect is similar to that observed in ordinary soft iron.

crystal boundaries have any effect on the value of the Hall coefficient.

An absolute determination of the Hall coefficient in aluminium is, however, valuable owing to the uncertainty that exists concerning its magnitude. For some time, the value generally accepted for the Hall effect in aluminium was about $3{\cdot}9\times10^{-4}$, but Smith * in 1910 obtained a lower value of $3{\cdot}2\times10^{-4}$. Smith, however, states that the aluminium used by him for this determination was of unknown origin and that impurities may have influenced his results.

A little later, Alterthum † published a paper in which he quotes $3{\cdot}9\times10^{-4}$ as the value of the Hall coefficient for aluminium at room temperature. However, during the course of his paper, Alterthum points out that on increasing the primary current from 1 ampere to about 1·5 amperes the value obtained was $3{\cdot}2\times10^{-4}$, which agrees with Smith's results. Raethjen ‡ recently examined the effect in aluminium foil, and obtained a value of $3{\cdot}43\times10^{-4}$ for the Hall constant. It is therefore evident that the value of the Hall coefficient for aluminium is somewhat uncertain.

Description of Apparatus and Method.

It has been proved experimentally that for a given metal the Hall electromotive force E is given in absolute units by the formula $E=\frac{RHI}{d}$, where H is the magnetic field in gauss, I is the current in absolute units, d is the thickness of the plate in cms., and R is the Hall coefficient, which in general is a function of the temperature and of the strength of the field.

Aluminium happens to have a very low coefficient of the order of 3×10^{-1}; and since the specimens used in the present experiments have an average thickness of ·3 cm., it follows from the above formula that for a current of 4 amperes and a magnetic field of about 6000 gauss the Hall potential difference is an extremely small quantity of the order of $2{\cdot}4\times10^{-8}$ volt. A very sensitive instrument is therefore required for the measurement of such a small potential difference, and for this purpose a delicate Paschen galvanometer made by the Cambridge Scientific Instrument Company was used.

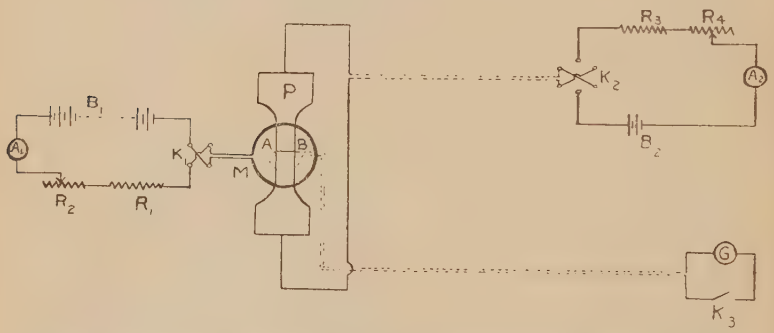
* Phys. Rev. xxx. p. 1 (1910).
† *Ann. d. Phys.* (4) xxxix. p. 933 (1912).
‡ *Phys. Zeits.* xxv. pp. 84–89 (1924).

The arrangement of the apparatus is shown in fig. 1, in which P represents one of the aluminium specimens.

The current through the specimen is supplied by a battery B_2 consisting of two storage cells. The remainder of the circuit consists of a rheostat R_3, a fine adjustment rheostat R_4, a reversing key K_2, and a Weston ammeter A_2, which had been calibrated against a large Weston standard ammeter, whose indications are correct to within one-tenth of 1 per cent. As the Weston ammeter A_2 enables the current to be read to within one part in 1200 of the current employed, the primary current through the plate could be measured correctly to within one-tenth of 1 per cent.

The specimen P was placed in a magnetic field, which was produced by a large circular electromagnet. The current through the coils of the magnet was supplied by the mains

Fig. 1.



from a storage battery B_1. A resistance frame R_1, an ammeter A_1, a fine adjustment rheostat R_2, and a reversing key K complete the magnet circuit. The magnetic fields corresponding to different currents through the coils of the electromagnet were measured by means of a Grassot fluxmeter and search coil. The absolute value of the magnetic field corresponding to a current of 2 amperes passing through the electromagnet was determined by means of a delicate ballistic galvanometer and a carefully constructed search coil whose mean area could be readily measured. In this way the corrections to be applied to the fluxmeter readings were determined, and the magnetic field measurements are considered to be correct to within about one-half per cent.

In fig. 1, K_3 in the secondary circuit represents a copper key and G represents the Paschen galvanometer. The galvanometer was mounted on a stone pillar, which was built into the concrete foundations of the laboratory. The

magnet system of the galvanometer was suspended between two pairs of coils, which could be connected in series or in parallel as required. When the coils were connected in series, as in the present experiments, the resistance of the galvanometer was 12·87 ohms. The terminals of the galvanometer were made of copper so as to eliminate thermoelectric effects. As the moving magnet system was easily influenced by external magnetic fields, it was found necessary to enclose the galvanometer in a double shield of soft iron. In this way the effect of external disturbing magnetic fields was very considerably reduced.

The Paschen galvanometer is characterized by its high sensitiveness corresponding to a comparatively quick period of motion of the magnet system. In the present experiments the control magnets were so arranged that for a period of about 3 seconds a microvolt applied to the terminals of the galvanometer produced a deflexion of about 38 cm. on a scale at a distance of 1 metre from the galvanometer.

The sensitiveness of the galvanometer varied slightly from day to day, probably owing to changes in the temperature of the room. The galvanometer was calibrated immediately before and after a series of readings of the Hall potential difference, and as was to be expected the calibration constant did not alter during that short interval of time.

The electromagnet was at a distance of $7\frac{1}{2}$ metres from the galvanometer, and was rotated into such a position that the direct effect of the permanent field of the excited electromagnet on the magnet system of the galvanometer was a minimum. This effect could be reduced to such an extent, that for a reversal of the magnetic field the change in the zero of the galvanometer as read on the scale 1 metre away was less than 1 mm. In this position of the electromagnet the sensitiveness of the galvanometer was found to be increased, and decreased respectively by about 1·2 per cent. on the application and reversal of the magnetic field for the maximum field employed. However, as will be shown later, a correction can be applied, if necessary, to eliminate any error on this account.

The galvanometer was connected to the specimen by means of long flexible wires, which were suspended overhead and were well insulated. The connecting wires were wound non-inductively, and kept taut to within a few inches of the galvanometer and aluminium plate respectively in order to avoid superimposed inductive effects in the galvanometer due to accidental vibrations.

The apparatus adopted for supporting the specimen in the

magnetic field consisted of a wooden frame, in which the specimen was rigidly supported in a vertical position in the air-space between the poles of the magnet. Brass clamps served as leads for the primary current, and the secondary electrodes consisted of spring copper contacts carried by thick strips of ebonite. In some cases the copper contacts were replaced by aluminium contacts, but the results were unaltered. By means of a screw arrangement the secondary electrodes could be moved along the edges of the specimen as required.

For a determination of the Hall coefficient an electric current was passed through the specimen, and the secondary electrodes were adjusted so that on closing the secondary circuit and reversing the current through the specimen, the deflexion indicated by the galvanometer was as nearly zero as possible. When this was the case, the secondary electrodes were practically on an equipotential line.

The magnetic field was then applied, and after a short interval of time, during which the inductive effects due to the application of the field had died down, the secondary circuit was closed and the reading on the scale of the galvanometer was observed. With the secondary circuit still closed, the primary current was quickly reversed and a second reading observed. The primary current was again reversed so as to pass in the original direction, and a third reading was noted. When the first and third readings agreed to within 1 mm., the mean of these two readings was taken and subtracted from the second reading to give a value of the deflexion produced by the field for a reversal of the primary current.

With the field still on, the primary current was reversed backwards and forwards so as to obtain several values of the deflexion, the mean of which shall be denoted by $2\theta_1$. Under good conditions it was found that for several reversals of the primary current through the plate the readings on the scale were identical for each particular direction of the primary current.

The secondary circuit was now opened, and the magnetic field was applied in the opposite direction. The primary current was again reversed a few times, in order to obtain an average deflexion $2\theta_2$ corresponding to the second direction of the field.

The mean of the two deflexions $2\theta_1$ and $2\theta_2$ on being halved gave a deflexion θ, which was proportional to the potential difference set up between the edges of the plate.

To be strictly correct, a small percentage correction should be applied so as to increase $2\theta_1$, and the same percentage correction so as to decrease the deflexion $2\theta_2$. This is due to

the fact that for one direction of the field the sensitiveness of the galvanometer was decreased by about 1·2 per cent. for the maximum field employed, whereas for the reverse direction of the field the sensitiveness of the galvanometer was increased by the some amount. Owing to the nature of the correction, however, it is clear that the result obtained on adding these slightly modified deflexions should agree with that obtained on adding the uncorrected deflexions. The difference between the results was calculated to be less than ·1 per cent. for the maximum field employed.

The galvanometer was calibrated under exactly the same conditions as existed for the determination of the Hall effect, and the potential difference required to be applied to the terminals of the galvanometer to produce a deflexion θ was determined. Owing to the resistance of the long leads in the secondary circuit not being negligible, this potential difference was multiplied by a factor 1·091 in order to give the potential difference between the edges of the plate.

The determinations of the Hall effect for the various specimens were carried out at room temperature, which was registered on an accurate mercury thermometer placed with its bulb against the plate. The plates employed in these experiments were of such dimensions that the current passed through them did not produce an appreciable rise of temperature.

It should be mentioned at this point that when a plate carrying an electric current is placed in a magnetic field, so that the lines of force are normal to the plane of the plate and to the direction of the flow of the current, a transverse galvanomagnetic temperature difference is set up between the edges of the plate. If the secondary electrodes are made of a different material from the plate itself, this temperature difference, which is known as the Ettingshausen effect, gives rise to a thermo-electromotive force which is superimposed on the Hall potential difference.

The Ettingshausen effect, however, for copper electrodes can be calculated to be only of the order of 3×10^{-11} volt* for the magnetic field and primary current employed in the present experiment, and can therefore (within the limits of experimental error) be neglected in comparison with the Hall potential difference. In addition, when aluminium electrodes were used, there was practically no difference of potential to be expected due to the Ettingshausen temperature difference.

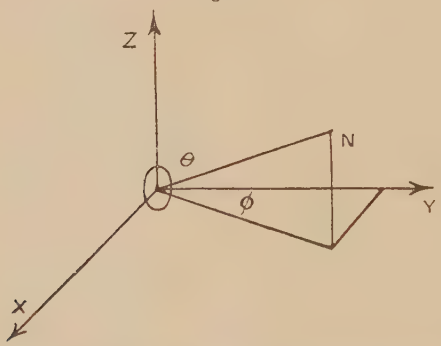
* Unwin found the Ettingshausen coefficient for aluminium at room temperature to be $+1{\cdot}06 \times 10^{-9}$.

A Determination of the Orientation of Crystals in Specimens.

The approximate orientation of the lattice planes of the single crystal in specimen A with respect to the face of the specimen was obtained by subjecting the crystal to an X-ray analysis. In specimen B the Hall effect was determined for the larger of the two crystals only, and this crystal was analysed by X-rays also. The method of procedure was somewhat similar to that described by Dr. Müller* in a paper published by him in 1924. The specimen under consideration was supported vertically and rotated in the path of a beam of X-rays from a copper target.

Following the method adopted by Dr. Müller, let X, Y, Z (fig. 2) represent the axes of a rectangular system of co-

Fig. 2.



ordinates in which the XY plane corresponds to the surface of the specimen, and the Z axis represents the direction of the long axis of the plate. The position of the line ON is then defined by the angles θ and ϕ, and the position of the cubic lattice is definitely fixed by the values of θ and ϕ for the normals to two known crystal planes.

In the present experiment the position of ON was determined only for the (111) planes in the lattice of each of the crystals A and B. Intense lines were obtained on the photographic plates, and from geometrical considerations were attributed to reflexions of the copper lines from the (111) planes of the crystals. From crystal B a reflexion was obtained from the (111) plane corresponding to the first order of the copper lines, but for crystal A a reflexion corresponding to the second order of the same lines was obtained.

* Roy. Soc. Proc. A, vol. cv. p. 500 (1924).

The value of θ was approximately determined from the nature of the photographs of these lines. In order to determine the angle ϕ it was necessary to know the angle of setting of the specimens for which the reflexions took place from the (111) plane. This was done by dividing into small ranges the whole of the range through which the specimen was originally turned, and determining for which of these ranges an intense (111) reflexion could be obtained. In this way the angle of setting for which the reflexion occurred could be determined to within a degree.

Experimental Results.

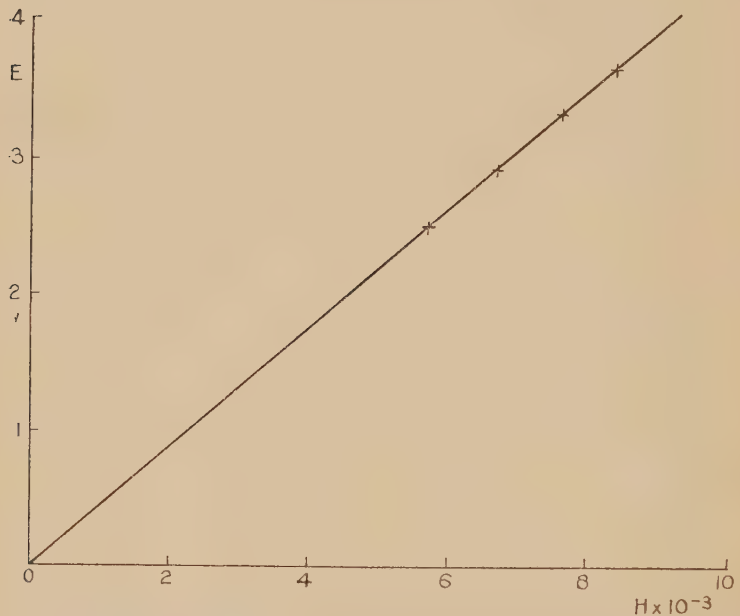
The Hall coefficient was determined for eight specimens of aluminium, which are represented in Table I. by the letters A, B, ... H. These specimens contained 99·6 per cent. aluminium, the chief impurity being silicon 0·19 per cent. and iron 0·14 per cent. Specimen A consisted of a single crystal 16 cm. in length and 2·5 cm. in width; specimen B contained two crystals of the same width (2·5 cm.) and of about 6 and 8 cm. in length respectively. The lengths of the crystals in specimen C were approximately 6·7 cm., 2 cm., and 8 cm., the width being 2·5 cm. in each case. The approximate average dimensions of the crystals contained in specimens D, E, and F were 1·8 cm. by 1·7 cm., 1 cm. by ·8 cm., and ·6 cm. by ·4 cm. respectively. Specimen G contained about 30 crystals per sq. cm., while specimen H, which was examined under a high-power microscope, was found to contain about 183 crystals per sq. mm.

The Hall potential difference in these specimens was measured for magnetic fields ranging from 5724 gauss to 8414 gauss. The current passed through the plate for each determination of the Hall coefficient was 3·923 amperes. The deflexions produced in the present experiments for a reversal of the Hall e.m.f. ranged from 1·36 cm. for the lowest magnetic field to 2·83 cm. for the highest magnetic field. These deflexions could be read to one-tenth of a millimetre on the scale of the galvanometer.

A graph was plotted for each specimen, showing the relation between the Hall potential difference and the magnetic field employed. A graph for crystal A is shown in fig. 3, where the ordinates represent the Hall e.m.f. in absolute units, and the abscissæ represent the field in gauss. From fig. 3 it is seen that the Hall potential difference is proportional to the magnetic field.

Similar graphs were obtained for each of the other specimens.

Fig. 3.—Specimen A.



The results of the investigation of the Hall effect for each of the specimens are as follows:—

TABLE I.

I = ·3923 absolute units.
H = 8414 gauss.

Specimen.	Number of grains per mm.²	*d*, in cm.	Temperature.	E, in absolute units.	R × 10⁴.
A	0·00025	0·3147	15·8° C.	3·61	−3·44
B	0·00057	0·3150	16·4 „	3·59	−3·43
C	0·00072	0·3140	11·0 „	3·60	−3·42
D	0·0032	0·3114	15·2 „	3·66	−3·45
E	0·0125	0·3065	15·4 „	3·73	−3·46
F	0·042	0·3090	13·0 „	3·65	−3·42
G	0·3	0·3010	12·8 „	3·77	−3·44
H	183	0·3161	15·6 „	3·60	−3·45

In Table I., E is the value in absolute units of the potential

difference for a magnetic field of 8414 gauss, and R is the value of the Hall coefficient calculated from the formula $R=\frac{Ed}{IH}$. The negative sign attributed to the coefficient R means that the Hall effect in aluminium is in the same direction as that in bismuth.

An examination of Table I. shows that the values of the Hall coefficients for all the specimens are in good agreement with each other. the mean value of the constant being $3{\cdot}44\times10^{-4}$ at a mean temperature of 14·4° C. The Hall coefficient was also determined for another plate of aluminium of thickness ·2605 cm., and for which the aluminium content amounted to at least 99·6 per cent. The Hall coefficient for this sample of aluminium was also found to be $3{\cdot}44\times10^{-4}$, a value which is in good agreement with that obtained for each of the other specimens investigated. It is interesting to note that this value of the Hall coefficient for aluminium only differs by about ·3 per cent. from that obtained by Raethjen *.

In order to compare the result obtained for aluminium with that obtained for a specimen of different material, the Hall coefficient was determined for a plate of electrolytic copper of the highest purity of thickness, ·150 cm. The value of the coefficient for copper was found to be $5{\cdot}27\times10^{-4}$ at room temperature (21° C.), and this value agrees well with the value ($5{\cdot}28\times10^{-4}$ at 18° C.) which was obtained by Alterthum †.

The results of the X-ray analysis in the case of the two specimens A and B are set down in Table II., where θ and ϕ are the angles referred to previously in connexion with fig. 2.

TABLE II.

Specimen.	θ.	ϕ.
A	86°	60°
B	68°	80°

These X-ray investigations do not lay claim to any great accuracy, but from the approximate results obtained it can be stated that the orientation of the crystal lattice with respect to the surface of the specimen differs in the case of the two crystals examined.

Although there is a difference in the orientation of the crystals, it is clear from Table I. (A and B) that the Hall

* *Loc. cit.*
† *Loc. cit.*

coefficient is the same in both cases, the small difference in the results being easily accounted for by experimental error. Since the primary current passes in a direction parallel to the surface of the specimen, it appears that the orientation of the lattice planes of the crystal with respect to the directions of the primary current does not in any way influence the Hall effect.

An examination of Table I. also shows that the Hall coefficient is the same within experimental error for all the crystalline aggregates, however large the number of crystals and the number of boundaries that exist in the specimen. Crystal size therefore has no influence on the magnitude of the Hall effect.

Summary.

1. The Hall coefficient has been determined for eight specimens of single and aggregate crystals of aluminium for a current of 3·923 amperes and for magnetic fields ranging from 5724 to 8414 gauss.

2. The Hall coefficient in aluminium is independent of crystal size.

3. The Hall coefficient is independent of the orientation of the lattice planes in the crystal with respect to the primary current.

4. The absolute value of the Hall coefficient for aluminium is $3{\cdot}44 \times 10^{-4}$.

I wish to express my gratitude to Professor E. J. Evans for his valuable advice, and to both Mr. W. Morris-Jones and Professor E. J. Evans for the use of their X-ray apparatus.

September 1927.

CXVIII. *On the Silvering of Glass Plates for Optical Instruments.* *By* J. J. Manley, *M.A.* (*Fellow of Magdalen College, Oxford*) *.

THE difficulties attending the preparation and renewal of plane-mirrors, such as those used in a Michelson interferometer, are well understood. Actual silvering is readily accomplished, but a chief difficulty arises from the uncertainty

* Communicated by the Author.

of obtaining a film sufficiently coherent and firm to endure the necessary polishing. Repeated failure led me to try some modifications of the usual procedure. Success was ultimately attained in two different ways, which are as follows :—

Method 1.—The glass plate, having been made chemically clean, is covered with distilled water and the containing-vessel placed in ice ; the measured portions of the two silvering solutions are also similarly cooled. In due time the water is poured away from off the glass plate and the vessel at once replaced in ice. Next, the two ice-cold solutions are rapidly mixed and immediately introduced into the vessel containing the plate to be silvered. Silvering proceeds slowly, and apparently in consequence of this the film acquires a firmness rarely attained at ordinary temperatures. After some 8 or 10 hours the plate is removed from the bath, then washed and dried, and finally polished in the usual manner.

Method 2.—According to the second plan, whereby the lengthy and tedious process of polishing is eliminated, the silvering is effected at the prevailing temperature of the room. It is allowed to proceed for from 10–15 minutes only. When the plate has been immersed for the appropriate time a gentle stream of water is passed through the bath for some minutes. The silvering is thus arrested and the plate partially washed. Lastly, the plate is rinsed a few times with distilled water and then set up vertically upon white blotting- or filter-paper. Thus the mirror is rapidly dried and so made ready for immediate use.

Prepared according to method 2, the silver surface possesses a high reflecting power and scratches are entirely absent. It will, however, be obvious that such a mirror, the silver film of which has marked tenuity, must be handled with care and fingering avoided ; but given proper treatment the permanence of the mirror is quite normal. The operation of renewing the reflecting silver film is simple in character and quickly performed, and the preparation of a new mirror is a commonplace, requiring but little experience or skill.

CXIX. *The Accuracy of the Monochord as a Measurer of Frequency.* By GEORGE E. ALLAN, *D.Sc., Lecturer on Applied Physics, Glasgow University* *.

CONTENTS.

Introductory.
Equation of motion of vibrating wire.
Corrections of Seebeck, Donkin, and Schaefer.
Apparatus: Monochord, standard metre, lead weights, standard vibrators, wire.
Monochord observations.
Effect of temperature on glass rule, forks, and wire.
Effect, on tension, of weight of monochord wire and upthrust on lead weights.
Effect of tension on linear density of wire.
Calculation of the Taylor frequency. Tables.
Form of correction. Logarithmic graphs.
Values found for m, c, p, q, and K.
Final form of correction.
Discussion.

ALTHOUGH the monochord is said to have been in use in the time of Pythagoras †, the elementary laws of vibrating strings were not made generally known till 1636, when Mersenne published them in a work entitled 'L'Harmonie Universelle.' These laws, expressed separately by Mersenne, were deduced as a whole from dynamical principles by Brook Taylor, who published them in his book on the 'Method of Increments' in 1715.

Galileo in 1638, Newton, Euler in 1729, D'Alembert in 1747, and Daniel Bernoulli in 1755 ‡ are also said to have studied the problem of vibrating strings.

When a uniform wire, of length l and linear density ρ_1, is subjected to tension T, the frequency of its fundamental vibrations, as expressed by Taylor's formula, is

$$n = \frac{1}{2l}\sqrt{\frac{T}{\rho_1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The more complete equation of motion of the vibrating string indicates that Taylor's formula is not exact, inasmuch

* Communicated by the Author.

† Helmholtz, 'Sensations of Tone,' 2nd English edition, p. 14 (1885).

‡ Rayleigh, 'Sound,' vol. i. p. 181. "It is to Daniel Bernoulli that we owe the general solution of the string equation."

as it makes no allowance for the "rigidity" of the wire. The equation may be written *:

$$\frac{d^2y}{dt^2} = \frac{T}{\rho_1}\cdot\frac{d^2y}{dx^2} - \frac{k^2E}{d}\cdot\frac{d^4y}{dx^4}, \quad . \quad . \quad . \quad . \quad (2)$$

where k is the radius of gyration of the section of the wire, E is Young's modulus, and d the volume density of the material of the wire. The last term in the equation introduces the correction for the resistance to bending, and the corrected frequency of the string then becomes †

$$n = \frac{1}{2l}\sqrt{\frac{T + EI\pi^2/l^2}{\rho_1}}, \quad . \quad . \quad . \quad . \quad (3)$$

where I is the moment of inertia of the cross-section of the wire. This correction is never applied in the ordinary use of the monochord, a fact which aids in causing the instrument to be regarded as a somewhat inaccurate means of measuring frequencies within the musical range.

A. Seebeck refers ‡ to Savart's correction for the rigidity of the wire, and to Duhamel's attempt to deduce the correction from theory. Seebeck also gives a form of correction which may, for our purpose, be modified so that in terms of the above symbols the observed frequency requires the addition of the quantity

$$\text{constant} \times \frac{n^2\rho_1^{\frac{3}{2}}}{T},$$

where n is the frequency of the perfectly flexible string. He states that this correction may not be neglected in exact monochord work, and gives its amount in one instance as 1 vibration in 127, as observed in some tests with a thin steel wire.

W. F. Donkin § gives a correction which may be similarly reduced to the form

$$\text{constant} \times \frac{n^3\rho_1^3}{T^2},$$

in which n is the frequency if the wire were perfectly thin. Schaefer's correction is the same as Donkin's. Donkin remarks that Seebeck found his correction to agree with experiment when the ends of the wire were clamped.

* See, for example, H. Lamb, 'Sound,' p. 132.
† O. Schaefer, *Ann. d. Physik*, vol. lxii. p. 156 (1920).
‡ *Ann. d. Physik u. Chemie*, vol. lxxiii. pp. 442–448 (18 8)
§ 'Acoustics,' 2nd edition, p. 179 (1884).

Donkin also found that his own form of the correction agreed with experiment in the case of a wire stretched over bridges *, but he gives no numerical data.

Both of the above authorities agree that the frequency as calculated by Taylor's formula is too low, that the deviation from the true frequency increases with the frequency and with the linear density, but diminishes with increased tension. These general conclusions are cited in the text-books on Sound by Rayleigh, Barton, and Lamb. The last-named author points out that the uncertainty of the correction for resistance to bending arises because of the uncertainty as to the nature of the terminal conditions of the wire. A wire where it passes over a bridge cannot be accurately regarded, he points out, as merely supported or as clamped.

Numerous researches have been made in which the monochord has played a part †; yet, so far as is known to the writer, no systematic experimental test of the monochord correction has been hitherto carried out.

The observations recorded here were made for the purpose of determining the magnitude of the correction and its dependence on frequency, linear density, and tension. Let n be the value of $\frac{1}{2l}\sqrt{\frac{T}{\rho_1}}$, or the Taylor frequency, and N the true frequency of the wire, then

$$N = n + \delta n, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where δn is the correction to be sought.

Apparatus.—Observations were made by means of a vertical monochord to which steel wires were attached and kept in definite tension by slotted weights placed on a brass

* *Loc. cit.* p. 187.

† J. Blyth, "Electric Sonometer," R.S.E. Proc. vol. xi. p. 28 (1880–81).
Barton and his co-workers, Phil. Mag. July 1905, p. 149; also Sc. Abstracts, 1907–12.
C. V. Raman, Phys. Rev. March 1911, p. 309. Motion at the nodes.
J. E. Ives, Phil. Mag. June 1911, p. 742. String in viscous medium.
J. A. Fleming, Phys. Soc. Proc. 1913. Loaded string and electrical analogue.
Kenelly and Manneback, Sc. Abstract No. 1915, Nov. 1921. Application of electric sonometer.
O. Schaefer, *loc. cit.* Measurement of expansion by monochord.
S. Ray, Phys. Rev. July 1926, p. 229. Investigation of wave-velocity.

carrier hung from the lower end of the wire. The wire made contact with two metallic bridges, and, as the upper bridge projected slightly beyond the lower one, satisfactory contact of the wire with both bridges was made by tilting the frame of the monochord back through about 1°. The length of the wire between the lower fixed bridge and the upper adjustable bridge was determined with a standard glass metre scale divided into centimetres and millimetres. The upper bridge had a screw for fine adjustment, and pads of cotton wool were used to stifle the vibrations of those parts of the wire which lay beyond the bridges. A small rimmed shelf below the lower bridge and a metal strap near the top of the monochord were fitted to carry the glass rule, so that the scale, when in use, was in contact with the wire, and the errors of parallax to which the readings of the bridge positions were liable were reduced to a negligible quantity. Length readings could thus be conveniently and accurately estimated, with the aid of a lens, to 1/10 mm. By making 10 cm. the minimum length observed, an accuracy of at least 1 in 500 was obtained in the measurement of the length l.

The lead weights were about 500 gm. each, and the carrier weighed 169·4 gm. One lead weight, used as a standard, was carefully weighed, and the others were determined in terms of this standard.

The effect on the tension of the weight of the monochord wire below the upper bridge is small and variable. If the length of wire below the lower bridge is L, and W gm. is the weight supported, the tension is expressed accurately enough by

$$T = W + \rho_1(L + \tfrac{1}{2}l) - 0{\cdot}108\,\frac{W}{1000}, \quad . \quad . \quad . \quad (5)$$

where it is taken that the upthrust on the lead weights due to air displaced is 0·108 gm. wt. per kilo. of lead. Since the greatest error introduced by neglecting the two effects mentioned was 1 in 7000, namely in the case of the thinnest wire when carrying the smallest weight, these two sources of error were not taken into account, and it was found sufficient to express the other tensions to the nearest gramme.

Standard Vibrators.—The standards of frequency consisted of three forks of respective frequencies 255·6, 514·2, and 1024. Of these, the first and third were made by Kœnig of Paris; the highest fork was of massive form and was in good condition, and was assumed to be correct at

14° C., a little over the average temperature of the tests. When the second and third forks were sounded together beats were heard which had a frequency of 4·4 per second. By the use of small rubber bands as loads, the octave of fork No. 2 was found to have the higher pitch, and the frequency of the fundamental of this fork, as found from the beats, was 514·2. Forks Nos. 1 and 2, when sounded together, gave three beats per second, No. 2 being again higher in pitch, and a value 255·6 was found for the frequency of No. 1 fork.

Wire.—Ordinary steel piano wire was used in various sizes. The observations refer to wires having approximate linear densities, etc., as given in the following table. The diameters, as found by screw-gauge, were not always in conformity with those of the standard wire gauge system, and in nearly all cases there was a tendency to ellipticity of section. When not in use, the hanks of wire were kept in a tin box containing a quantity of dry slaked lime to prevent the rusting of the wires. The wires gradually rusted when hanging on the monochord, but readings were taken while the wires were fresh in order to discount this effect.

TABLE I.

Dimensions of Wires.

S.W.G. No.	Mean diameter. mm.	Linear density. gm./cm.	Approximate breaking-weight. kgm.
32	0·277	0·004930	17·7
28	0·351	0·007656	26·3
26	0·456	0·01278	40·0
23	0·616	0·02318	78·5

The figures in the last column are from one-reading tests, and are included to give a rough idea of the limiting tension which may be applied to these wires.

Monochord Observations.—Using a given wire and fork, a series of observations was taken for tensions varying from 668·9 gm. to 11,002 gm. weight, in all nine different tensions being employed. These tensions are specified in Table II.

TABLE II.—Monochord lengths, Taylor frequencies, and monochord errors. $\rho_0 = 0{\cdot}0041$ 30 gm. per cm.

Graph.	T.	668·9 2·8254	1168 3·0675	1667 3·2219	2669 3·4263	4164½ 3·6195	5668 3·7534	7175 3·8558	8684 3·9387	11002 4·0415
A 514·2	l	11·60	15·05	17·89	22·54	28·08	32·76			
	n	497·4	506·8	509·4	511·8	513·4	513·7			
	δn	16·8	7·4	4·8	2·4	0·8	0·5			
	$\log \delta n$	1·2253	·8692	·6810	·3802					
B 1024	l	...	...	9·10	11·41	14·17	16·50	18·54	20·40	22·95
	n	...	...	1001·5	1011·1	1017·4	1019·9	1021·8	1022·1	1023·6
	δn	...	...	22·5	12·9	6·6	4·1	2·2	1·9	0·4
	$\log \delta n$	...	...	1·3522	1·1106	·8195	·6128	·3424	·2788	

In the table above, the first column contains the letter by which the graph is denominated and the frequency of the standard fork. At the top are given the tensions in grammes and, for convenience, their logarithms. The spaces below contain the monochord lengths in cm., the Taylor frequencies, the monochord errors and their logarithms. In the graphs $\log \delta n$ is plotted against $\log T$. No points are plotted for errors less than unity.

TABLE III.—$\rho_0 = 0{\cdot}007656$ gm. per cm.

Graph.	T. $\frac{m}{n}$ 668·9	1168	1667	2669	4164	5668	7175	8684	11002
C 255·6	l	18·66	24·28	28·86	36·36					
	n	248·2	252·0	253·4	254·6					
	δn	7·4	3·6	2·3	1·1					
	$\log \delta n$	·869	·556	·362	·041					
D 514·2	l	...	12·35	14·53	18·23	22·64	26·36	29·60	32·56	
	n	...	495·5	503·2	507·7	510·8	512·0	513·2	513·4	
	δn	...	18·7	11·0	6·5	3·4	2·2	1·0	0·8	
	$\log \delta n$	...	1·272	1·041	·813	·532	·342	0		
E 1024	l	...	...	...	9·33	11·48	13·33	14·95	16·43	18·18
	n	...	...	...	992·0	1007·3	1012·4	1016·1	1017·5	1018·7
	δn	...	...	...	32·0	16·7	11·6	7·9	6·5	5·3
	$\log \delta n$	...	...	...	1·505	1·223	1·065	·898	·813	·724

TABLE IV.—ρ_0=0·01278 gm. per cm.

Graph.	T.	668·9	1168	1667	2669	4164	5668	7175	8684	11002
F 255·6	l	...	19·25	22·63	28·35	35·19	40·97			
	n	...	245·9	249·9	252·5	254·1	254·7			
	δn	...	9·7	5·7	3·1	1·5	0·9			
	log δn	...	·987	·756	·491	·176				
G 514·2	l	...	...	...	14·40	17·77	20·56	23·06	25·30	
	n	...	...	...	497·2	503·3	507·6	509·4	510·8	
	δn	...	...	...	17·0	10·9	6·6	4·8	3·4	
	log δn	...	...	...	1·230	1·037	·820	·681	·532	
H 1024	l	...	...	...	...	9·15	10·51	11·74	12·85	
	n	...	...	...	...	977·4	993·0	1000·5	1005·8	
	δn	...	...	...	...	46·6	31·0	23·5	18·2	
	log δn	...	...	...	...	1·668	1·491	1·371	1·260	

TABLE V.—ρ_0=0·02318 gm. per cm.

Graph.	T	668·9	1168	1667	2669	4164	5668	7175	8684	11002
I 255·6	l	...	...	...	21·70	26·58	30·76	34·56	37·86	42·49
	n	...	...	...	245·0	249·8	251·9	252·3	253·4	254·2
	δn	...	...	...	10·6	5·8	3·7	3·3	2·2	1·4
	log δn	...	...	...	1·025	·763	·568	·519	·342	·146

With a given tension, six independent determinations were made of the monochord length of wire in unison with the fork, the bridge being put out of adjustment between the readings. In many cases the process was carried through three times, and in a few cases four times. The tuning was done by any or all of the methods: (*a*) by sense of tune, (*b*) by adjustment for maximum resonance, and (*c*) by reducing the beats to zero. The observations and results are given in Tables II. to VI. and in the accompanying graphs.

Calculation of the Taylor Frequency.—Before applying Taylor's formula, it is necessary to consider whether the readings require to be standardized for changes of temperature. Such changes will affect the standard metre, the standard forks, and the monochord wire. The range of temperature within which the tests were carried out was from 8°·5 to 17°·5 C., but most of the tests were made at temperatures between 11° and 13° C., and no corrections were applied for temperature effects. It is well known that the frequency of a fork undergoes a slight diminution with rise of temperature according to the formula

$$N = N_0(1 - \alpha t),$$

where $t°$ C. is the temperature at which the frequency of the fork is N, and α is a coefficient which, for small temperature range, may be taken as 0·0001 *. A change of temperature of 10° would thus alter the frequency by about 1 in 1000. An endeavour was made to keep this error as low as possible by taking the tests when the room-temperature was between 11° and 13° C.

Effect of Tension on Linear Density.—Let a uniform steel wire of circular section, of radius r and of length l when unstretched, have mass m and density d. Then its linear density is given by

$$\rho_0 = \frac{m}{l} = \pi r^2 d. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

When the wire is under tension T, let its length become $l + \delta l$. Its linear density ρ_1 is now

$$\rho_1 = \frac{m}{l + \delta l}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence

$$\frac{\rho_1}{\rho_0} = \frac{l}{l + \delta l} = 1 - \frac{\delta l}{l} \text{ nearly.}$$

* E. C. Woodruff, Phys. Rev. xvi. pp. 325–55 (June 1903).

Also, by Hooke's law,

$$E\frac{\delta l}{l} = \frac{T}{\pi r^2} = \frac{Td}{\rho_0}, \text{ by (6).}$$

Therefore

$$\frac{\rho_1}{\rho_0} = 1 - \frac{Td}{E\rho_0} \text{ nearly,}$$

or

$$\rho_1 = \rho_0 - \frac{d}{E}T \text{ nearly. . . . . (8)}$$

From this approximation it appears that the correction is constant in amount for a given tension, and can be determined once for all for the series of tensions employed.

If we take for steel the values

$$d = 7{\cdot}7 \text{ gm. per c.c.}$$

$$E = 2{\cdot}2 \times 10^9 \text{ gm. wt. per sq. cm.,}$$

$$\rho_1 = \rho_0 - 3{\cdot}5 \times 10^{-9} \times T,$$

where T is expressed in grammes weight. For a No. 32 wire under 8700 gm. weight tension, the correction amounts to more than 1 in 200. Lengths of the respective wires were accordingly measured under quite low tension, and weighed on a balance which had a sensitiveness of 0·20 mgm. per division. Tables were prepared giving the linear densities of each wire for the different tensions employed, and the Taylor frequencies were calculated by means of these tables, δn being then found from equation (4).

Form of the Correction.—Assume that the correction may be applied in the general form in which those of Seebeck and Donkin have been expressed, and let

$$\delta n = K\frac{n^p \rho_1^q}{T^m}, \quad . . . . . (9)$$

where K is a constant. Then it remains to find values of p, q, m, and K which will satisfy the experimental results. It is to be noted that here n is the Taylor frequency, which is the only frequency available from the observations when an unknown frequency is being determined.

Beginning with the tension, the powers of T which appear in the corrections of Seebeck and Donkin are respectively 1 and 2. Neither of these powers fits the experimental results.

Assume, then, that $\delta n \times T^m$ is constant for a given frequency, then

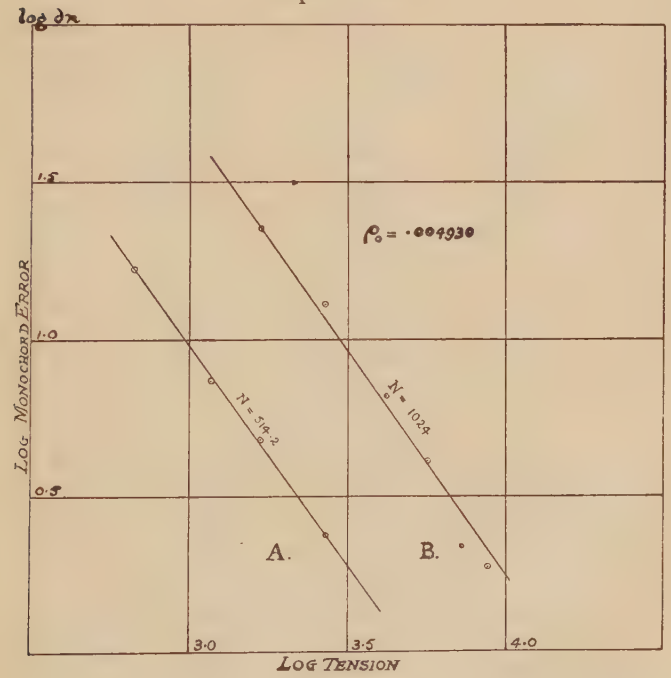
$$\log \delta n + m \log T = c, \quad . \quad . \quad . \quad . \quad (10)$$

and the graph of $\log \delta n$ and $\log T$ is a straight line of the type

$$y + mx = c.$$

The values of $\log \delta n$ were plotted against $\log T$, and straight lines were drawn through the mean positions of the points. An inspection of the graphs confirms the view that, apart from experimental error, the points lie on approximately

Graphs A and B.



parallel straight lines whose distance from the origin increases with the frequency and the linear density. The general conclusions of Seebeck and Donkin are thus verified within the scope of the experiments.

Value of m from the Graphs.—The power m was measured for each line from the ratio of the intercepts on the axes.

In general, the values differed from line to line, but an average has been taken as applicable over the whole range of observations.

Graphs C, D, and E.

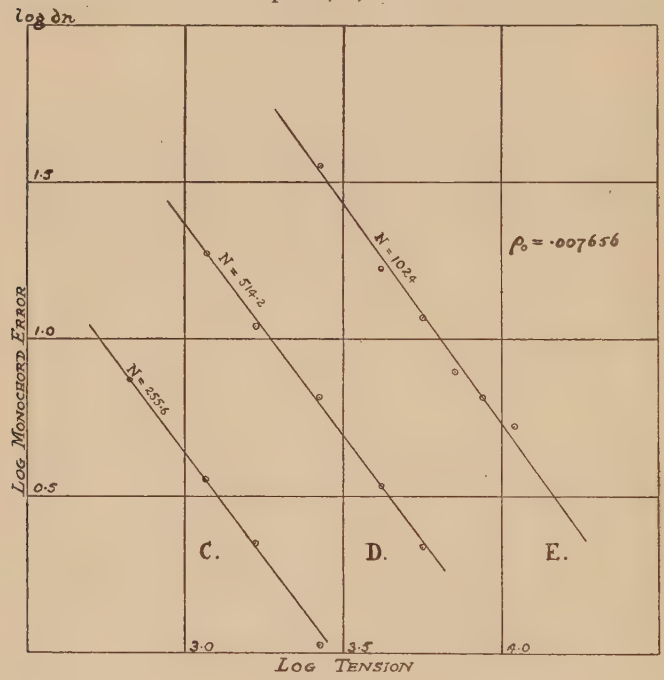


TABLE VI.

Values of m and c.

Graph.	Frequency.	Linear density.	m.	c.
A	514·2	·004930	1·406	5·072
B	1024	do.	1·420	5·719
C	255·6	·007656	1·297	4·733
D	514·2	do.	1·322	5·469
E	1024	do.	1·370	6·191
F	255·6	·01278	1·428	5·155
G	514·2	do.	1·412	5·940
H	1024	do.	1·284	6·627
I	255·6	·02318	1·357	5·714

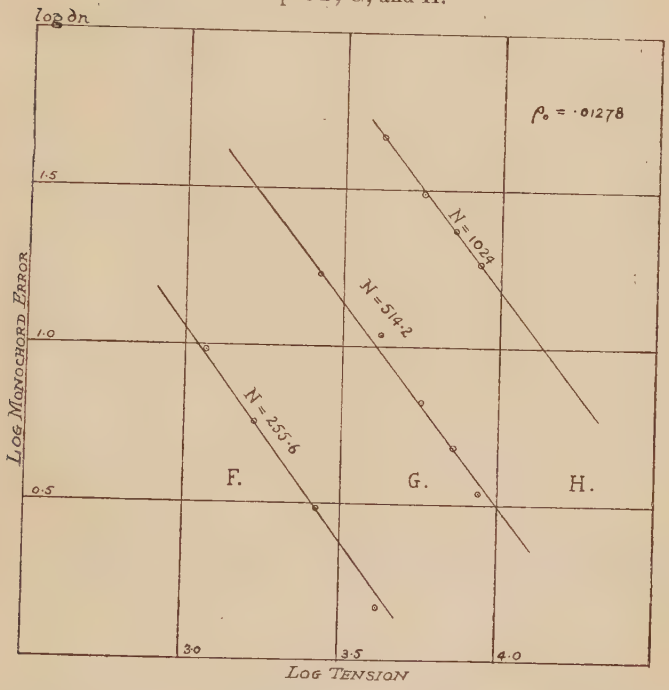
Mean $m = 1·366$

Values of c.—Placing in equation (10) the value found for m, along with a pair of values for $\log \delta n$ and $\log T$ respectively, mean values of c were found for each wire and each frequency. These mean values have been included in Table VI. above.

Evaluation of p, q, and K.—We get, from equations (9) and (10) above,

$$c = \log K + p \log n + q \log \rho_1. \quad . \quad . \quad . \quad (11)$$

Graphs F, G, and H.



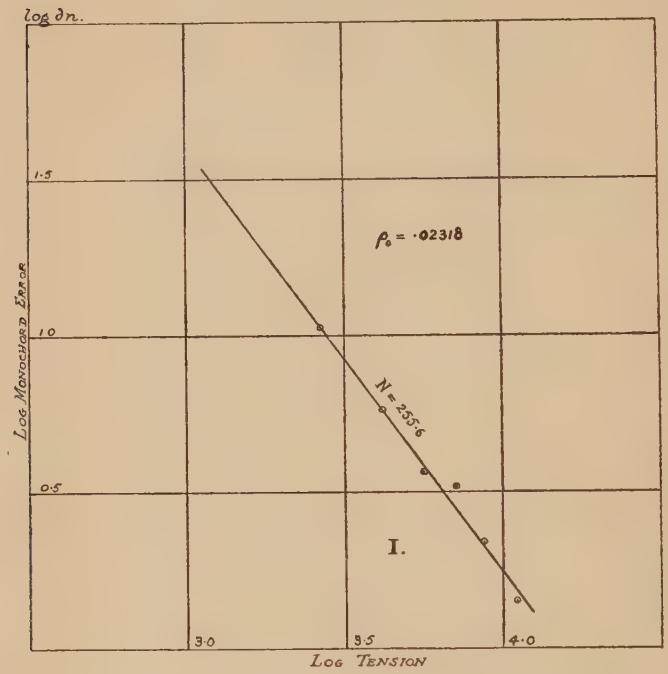
In this equation c and n are known, and if we employ the equation twice for the same wire with the same tension, but for different frequencies, K and $q \log \rho_1$ may be eliminated, giving

$$p = \frac{c_2 - c_1}{\log n_2 - \log n_1}. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Corresponding values for c and n were taken for graphs A and B, C and D, D and E, F and G, and G and H from

Tables II.–VI., and inserted in equation (12), the mean value found for p being 2·391.

Graph I.



In a similar manner, using the data for different wires with the same frequency and same tension, we get

$$q = \frac{c_2 - c_1 - p(\log n_2 - \log n_1)}{\log \rho_1'' - \log \rho_1'} \text{ *}, \quad . \quad . \quad . \quad (13)$$

where c_2 and c_1 refer to the values for, say, graphs D and A, and ρ_1'' and ρ_1' to the corresponding linear densities. Taking the appropriate values for graphs A and D, B and E, C and F, D and G, and E and H, twelve values of q were determined, of which the average was 2·070.

Value of K.—Substitution of the values found for c, p, and q in equation (11) gives log K. Here one value was

* The Taylor frequencies are not exactly the same.

found for each graph, and the average of the nine was $\log K = 3{\cdot}274$, from which $K = 1880$.

Final Form of the Correction.—The correction can now be stated in its numerical form, namely,

$$\log \delta n = 3{\cdot}274 + 2{\cdot}391 \log n + 2{\cdot}070 \log \rho_1 - 1{\cdot}366 \log T,$$

which is suitable for computation with four-figure logarithms.

Discussion.

In the determination of frequency by the monochord, the improvement to be obtained by using the correction stated above may be gauged if we consider first the degree of error involved in the use of Taylor's formula alone. With low tension the error may exceed 4 per cent., but with increased tension the error in measuring a low frequency, say round about 200 per second, may be reduced to the disappearing point. The correction is not important when low frequencies are measured with a thin wire under high tension, provided due allowance is made for the change of linear density with tension. With higher frequencies the error cannot be made to disappear, since, with the three largest wires used, the breaking weight is reached before the error is reduced to unity. This can be verified by noting where the graphs for $N = 1024$ cut the $\log T$ axis.

The wire No. 23 S.W.G. is too thick for monochord work. With thinner wires greater brilliance of tone is obtained; also the wires offer a greater length for measurement, and they respond visibly when in tune. As a measurer of frequency the monochord has a limited range of usefulness which may be regarded as including frequencies from 50 to 2000, the accuracy obtainable at the higher frequency being less than 1 in 500.

The above tests were made in the Applied Physics Department of the University of Glasgow, and the writer desires to thank Professor J. G. Gray for his friendly interest in the work.

July 10th, 1927.

CXX. *The Temperature-Electrical Resistivity Relationship in certain Copper Alpha Solid Solution Alloys.* *By* A. L. Norbury, *D.Sc.*, *and* K. Kuwada (*both of University College, Swansea*) *.

Experimental Methods.

THE alloys used were in the form of annealed wires (0·03 inch diam.). Their compositions are given in Table I. Their preparation is described in previous papers †. To measure their electrical resistivities at various temperatures, each wire was made into a spiral coil, about 1 cm. diam. by 4 cm. long, containing about 40 cm. of wire. A current of about 2 amps. was passed through each spiral via leads (about 30 cm. long) formed by the two free ends. A copper wire was fused on to each lead just outside the spiral. These two copper wires were connected to a Tinsley Vernier Potentiometer and the drop of potential compared with a known drop of potential in the main circuit. The arrangement was consequently similar to that in a platinum resistance pyrometer. The thermostats used were :—liquid air (−191°), solid CO_2 in alcohol (−78° to 0°), room temperature (17° to 21°), B.P. water (100°), B.P. naphthalene (218°), B.P. mercury (356°) and B.P. sulphur (444°) ‡. Each spiral and its leads was placed in a half-inch internal diameter glass tube closed at the lower end, which projected into the thermostat. Condensation of moisture at low temperatures caused errors, but this was overcome by drying and sealing up with paraffin wax.

Results obtained.

The results obtained are collected in Table I. and plotted in fig. 1, where it will be seen that a plotting of resistivity against temperature gives a linear relationship between −191° and 438° C., within the limits of experimental error, for all the alloys with the exceptions of the manganese-copper and nickel-copper alloys. The points for these alloys lie on curves which decrease in slope with increase in temperature. With these exceptions the linear relationship may be expressed by:

$$R_{t^\circ} = R_{0^\circ} + \alpha \times t^\circ \text{ C.} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

* Communicated by the Authors.

† Journ. Inst. Metals, vol. xxix. 1923 (ii.) p. 423. Phil. Mag. ii. p. 1188, Dec. 1923.

‡ The temperature in this thermostat was actually 438° C.

Table I.

Electrical Resistivities of Certain Annealed Copper Alpha Solid Solution Alloys at Temperatures between −191° and 438° C.

Added Element Weight per cent.	Electrical Resistivity (in microhms per cm. cube) at Certain Temperatures.									$R_{0°}$ *.	α †.
	Liquid air (−191°).	Solid CO_2 in Alcohol.		Room Temperature.		Water 100°.	Boiling-point of Naphthalene 218°.	Boiling-point of Mercury 356°.	Boiling-point of Sulphur (438°).		
		Sp. Res.	Temp.	Sp. Res.	Temp.						
Pure Cu.	0·35	1·07	−67°	1·70	20°	2·25	3·03	4·01	4·60	1·57	0·0066
Al. 1·92	5·03	5·95	−73	6·64	21	7·24	8·11	9·18	9·81	6·48	0·0076
„ 2·88	6·33	7·32	−72	8·05	18	8·75	9·64	10·62	11·49	7·90	0·0084
„ 3·82	7·52	8·59	−73	9·27	18	9·99	10·96	12·21	12·88	9·16	0·0085
Mn. 2·40	7·92	9·12	−72	9·85	20	10·39	11·09	11·89	12·32	9·70	not constant
„ 7·20	27·12	28·77	−72	28·88	20	29·15	29·53	29·73	30·12	28·92	not constant
Ni. 4·52	6·27	7·23	−70	7·91	17	8·47	9·38	10·31	10·89	7·80	not constant
„ 9·20	11·92	12·99	−68	13·58	17	14·23	14·91	16·05	16·61	13·48	not constant
Sn. 1·00	1·65	2·51	−70	3·13	19	3·71	4·48	5·51	6·07	3·01	0·0071
„ 2·03	2·53	3·71	−72	4·40	19	5·05	5·86	6·93	7·53	4·25	0·0074
„ 2·96	3·79	5·04	−68	5·65	18	6·30	7·13	8·18	8·75	5·53	0·0074
„ 3·88	5·30	6·34	−70	7·00	17	7·65	8·50	9·39	10·11	6·79	0·0075
Si. 0·93	7·72	8·83	−71	9·50	17	10·35	11·27	12·51	13·16	9·42	0·0085
„ 1·71	13·46	14·78	−58	15·24	18	16·36	17·15	18·39	19·33	15·22	0·0091
„ 2·71	18·72	19·89	−58	20·80	17	22·05	23·14	24·67	25·36	20·70	0·0107

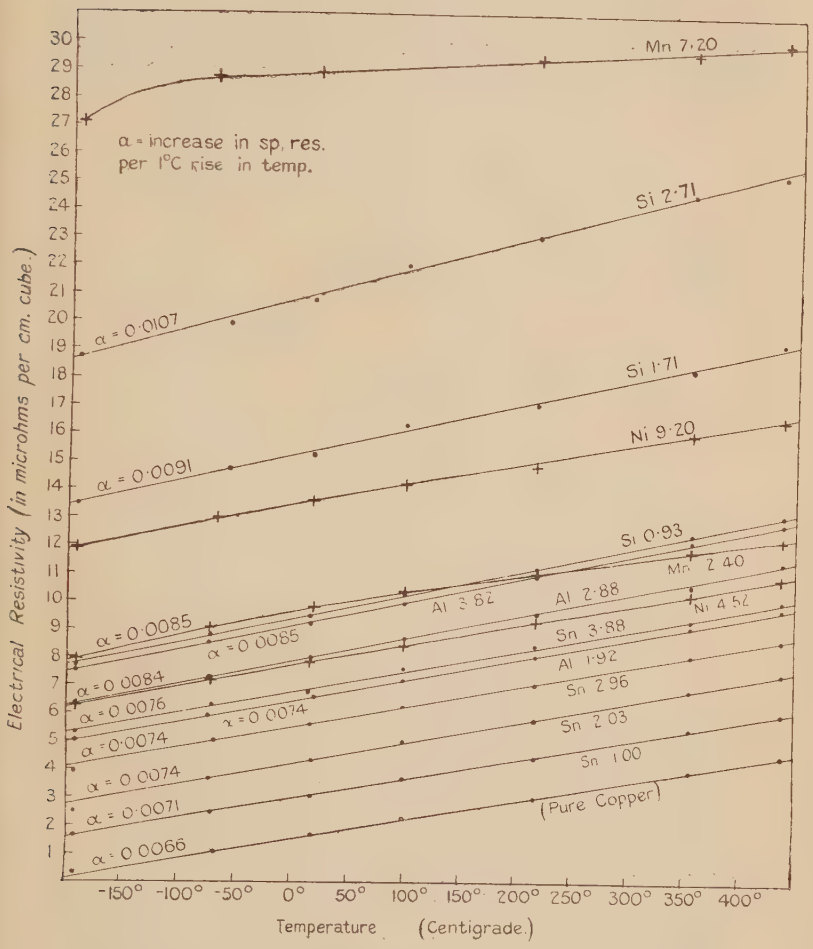
* $R_{0°}$ = specific resistivity at 0° C.

† α = increase in sp. res. per 1° C. rise in temperature for temperatures between −191° and 438° C.

(where R_t = sp. res. at $t°$ C. R_0 = sp. res. at 0° C., and α = increase in sp. res. per 1° C. rise in temperature).

It has previously been accepted that such lines, for dilute

Fig. 1.



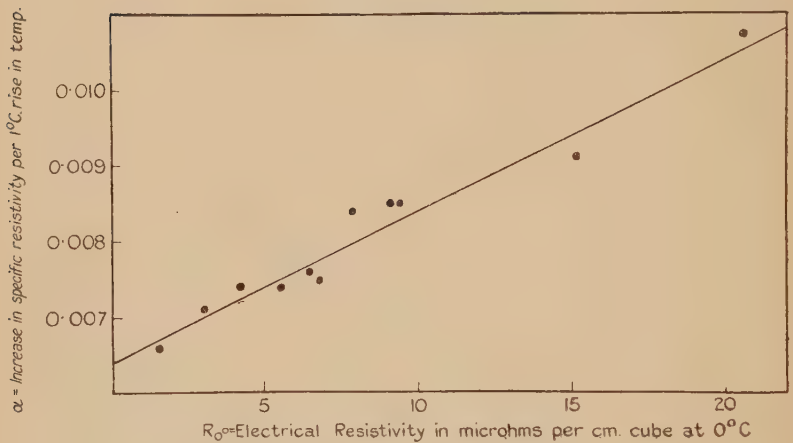
Electrical Resistivities of Certain Annealed Copper Alpha Solid Solutions at Temperatures between —191° and 438° C.

solid solution alloys, are parallel to one another, *i. e.* that they have a common value of α. A reference to the subject and to the work of Clay, Guertler, Bornemann, etc., will be

found in a previous paper by one of the authors *. The present data in fig. 1 show, however, that the lines are approximately, but not exactly, parallel to one another—in other words α is not the same for each.

By plotting the fig. 1 results on a large scale, values of α and $R_{0°}$ for each alloy have been estimated and have been included in Table I. If these $R_{0°}$ and α values are plotted against one another as shown in fig. 2, a linear relationship, within the limits of experimental error, is obtained, showing

Fig. 2.



Values of a plotted against values of $R_{0°}$.
(Relationship : $a = 0{\cdot}0064 + 0{\cdot}0002\ R_{0°}$.)

that α increases in value when $R_{0°}$ increases in value. The relationship in fig. 2 may be expressed by the equation :

$$\alpha = 0{\cdot}0064 + R_{0°} \times 0{\cdot}0002 \text{ microhms per cm. cube.} \quad . \quad . \quad \text{(ii.)}$$

Hence a combination of equations (i.) and (ii.) gives :

$$R_{t°} = R_0 + (0{\cdot}0064 + R_{0°} \times 0{\cdot}0002)\, t° \text{ C.}$$
microhms per cm. cube. . . . . (iii.)

which signifies that $R_{t°}$ (the sp. res. at any temperature $t°$ between $-191°$ and $438°$ C.) may be calculated from a knowledge of $R_{0°}$ † (the sp. res. at 0° C.), and that this

* Trans. Faraday Soc. vol. xvii. p. 257 (1921).

† By suitably modifying the equation the sp. res. at any temperature may be used as a basis for calculating the sp. res. at any other temperature between $-191°$ and $438°$ C.

equation holds for all the alloys used in the present research, with the exceptions of the manganese-copper and nickel-copper alloys.

The above results also have a bearing on the general relationship, found by one of the authors in a previous paper (*loc. cit.*), in which it was shown that the magnitudes of the "atomic effects" of solute elements in increasing the electrical resistivity of a metallic solvent were connected with the relative positions of the solvent and solute elements in the Periodic Table.

The bearing of the above results is that a higher or lower temperature of comparison than room temperature will give higher or lower values for the "atomic effects," but these will all be raised or lowered by the same percentage. Hence, a comparison of their relative "atomic effects" in a given solvent is independent of the temperature at which it is made.

The manganese-copper and nickel-copper alloys deviate somewhat from the above, since the comparison of their "atomic effects" is approximately, but not exactly, independent of the temperature of comparison.

In conclusion, the authors wish to thank Principal C. A. Edwards, D.Sc., for facilities for carrying out the present work and for his encouragement and advice; and acknowledge their indebtedness to the Royal Society Committee for a Government Grant.

CXXI. *Condenser Discharges in Discharge-Tubes.*—Part II. *The Intermittent Discharge.* *By* William Clarkson, *M.Sc., A.Inst.P., The Physical Institute of the University of Utrecht* *.

I. Introduction.

THE intermittent discharge has been the subject of wide study during the past few years [1].

Previous work has been largely on the timing relations. Both the empirical and the theoretical relations for the time of flash were quite early established [2], but it was found that if the sparking and the extinction potentials, or later even the maximum (peak) and minimum voltages as measured, were substituted in the relations, the timing agreement was not good.

* Communicated by Professor Ornstein.

Initially the time of duration of a flash was assumed to be negligibly small, but it was later seen that a lag at sparking was implied by certain phenomena and by timing graphs.

The large timing discrepancies at higher frequencies have been attributed [3] to "clear-up" phenomena. Though this was mainly true over the region studied, it is shown here that appreciable lags both at "build-up" and "clear-up" of a discharge must be considered in a complete explanation.

2. Methods.

Since all three variables—voltage, current, and time—were to be employed in calculations, it was necessary to determine their values accurately and to intercalibrate the various instruments used [4].

The capacities and the voltmeter were correct, and the shunted galvanometer was calibrated against the latter. All parts of the circuit were thoroughly insulated.

It was necessary to determine exactly what error was caused by the potential-drop in the diode filament of the diode-voltmeter combination. A rotating commutator showed that small errors could occur. Corrections, when necessary, were easily made.

Suitable allowance was made when the circuit current could not be maintained at the saturation value for the circuit diode employed.

When it was desired to eliminate the leakage due to photo-electric currents, the tubes were worked in partial or complete darkness. Circuit currents down to $0{\cdot}05\,\mu$A. could then be measured.

A standardized rotating commutator was found to give satisfactory results for frequencies intermediate between those timable on a stop-watch and those determinable by a monochord.

3. General Considerations.

Neglecting the discharge-period, the time of flash (T) is given by

$$T = C(v_m - V_N)/i, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where i is the charging current, C the capacity, v_m the "striking" potential, and V_N the minimum potential attained.

Actually, since lag was present, the increase of current to a maximum and its subsequent fall to zero is gradual, and there is an interval at the beginning of "build-up" and the end of "clear-up" when the charging current i exceeds

the discharge current I and the voltage rises, even though a discharge is passing. The maximum and minimum voltages, V_C and V_B respectively, will be attained when $i = I$ (fig. 1, *a*)[4].

The respective deviations of V_C and V_B from the starting voltage, ($\Delta_C = V_C - v_m$), and from that, V_N, to which the condenser would have fallen, ($\Delta_B = V_B - V_N$), will, of course, depend on the rate of charge (i/C) and on the current-time relations in discharge.

It is also apparent that a clear-up current may still be flowing when the corresponding striking voltage (v_m) as determined by threshold-current characteristic is reached. This is here denominated "overlapping"[5]. The reduction of v_m will become more pronounced as the time of flash is diminished.

Fig. 1 illustrates the phenomena just described. It will be seen that only the points V_C, i and V_B, i are known accurately, and that the values of v_m, i_m and v_n, i_n can merely be inferred.

4. V_C, V_B Variations.

These variations were systematically studied for constant capacity (C) and various currents (i), and *vice versâ*. V_C, V_B curves obtained under similar conditions were of the same form for all tubes. Actually these V_C, V_B, i and the V_C, V_B, C curves correspond very closely to V_C, V_B, n (frequency) and V_C, V_B, T curves respectively. It was found that if all results were plotted on an n or a T basis, curves of precisely similar form to those given were obtained.

These results suggest that the V_C, V_B phenomena arise universally from similar causes: a general solution should therefore be possible.

It was most convenient to study the V_C, V_B, n changes with C constant, i variable.

a. C *constant*, *i variable*.—The changes described here are for a steady increase of charging current (fig. 3).

A steady corona discharge was obtainable for a certain range of small currents. Though this range corresponded to the major part of the corona characteristic for very small capacities ($< 0{\cdot}001$ μF.), it was inappreciable for large values.

Corona flashes were then observed, with currents up to 1 μA., say, in the case of $C = 0{\cdot}1$ μF. Though very faint and slow at first, with V_C and V_B both of the value v_c (approx.), they became much quicker as i was increased,

and though V_C remained almost constant V_B fell rapidly, as in single flashes, and finally normal flashes occurred. The succession of corona flashes discharges preliminary to a normal flash, described on a previous occasion[4], would appear to be connected with lag phenomena of a more variable nature than present here.

Even with normal flashes V_C was approximately constant up to a frequency of 1–2 per second, but then rose in a regular manner, attaining, as a rule, a maximum (10–40 volts) at $n=20$, say (see figs. 5 & 6). dV/dn was then small, and at about $n=40$ V_C showed a progressive diminution, equalling v_e at about $n=100$ or so. The minimum value attained, generally with n equalling several hundreds per second, was frequently quite close to v_b in value. A steady discharge now occurred.

V_B changed in a reverse manner to V_C for normal flashes, being almost constant initially, then falling rapidly until attaining a minimum at about the maximum V_C, and finally rising slowly, with decreasing rate. It was generally approximately v_b just before the steady discharge was attained.

It is the purpose of this paper to show that the current-time relations in discharges, the "striking" and "clear-up" properties of the characteristic, and the variation of "build-up" with voltage serve to explain these phenomena, as well as those of single flashes. As is to be expected, the explanations developed here were found to apply to the other cases also.

b. V_e.—The voltage-time (V, t) relations assumed are given in fig. 1 (a), where the effect of a constant charging current, tending to produce a steady increase of voltage, is shown. The voltage increases slowly to a maximum (V_C at a time τ), and then falls at an ever increasing rate (v_n at time θ).

With the rate of build-up constant, *i. e.* duration of discharge, θ, constant, τ and hence Δ_C ($\propto \tau$ and i/C) will increase with, though not more slowly than, i. The ratio τ/θ will also increase regularly, and though almost zero initially will be approximately unity for large values of i/C[4].

Actually, however, the rate of build-up is not constant, but increases with voltage, and though the voltage it corresponds to in intermittence is indeterminate ($< V_C$, $> v_m$), θ certainly becomes rapidly smaller as i/C and hence Δ_C become greater. The general variation of the ratio τ/θ will be unaffected; thus τ will increase rapidly with i/C, attain a maximum, and then change in a similar manner to θ.

The resulting Δc, i curve will be doubly inflected as in figs. 5 and 6. Vc, almost constant for corona and for the

Fig. 4.

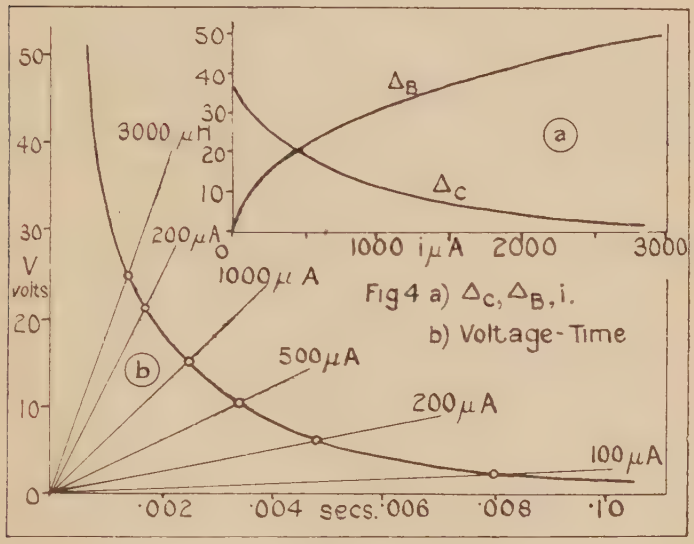
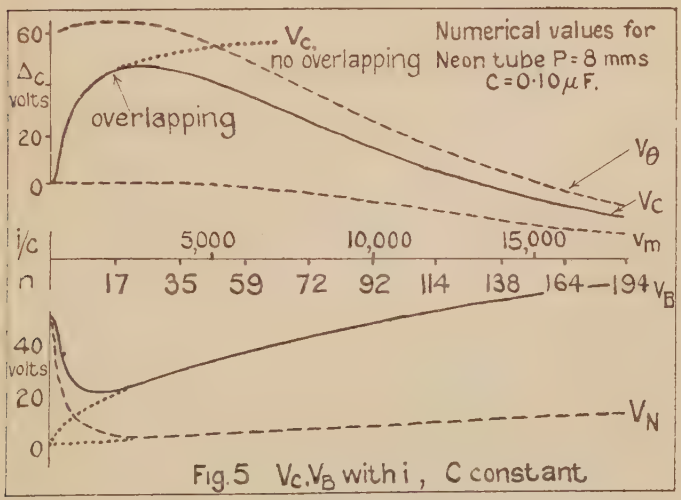


Fig. 5.

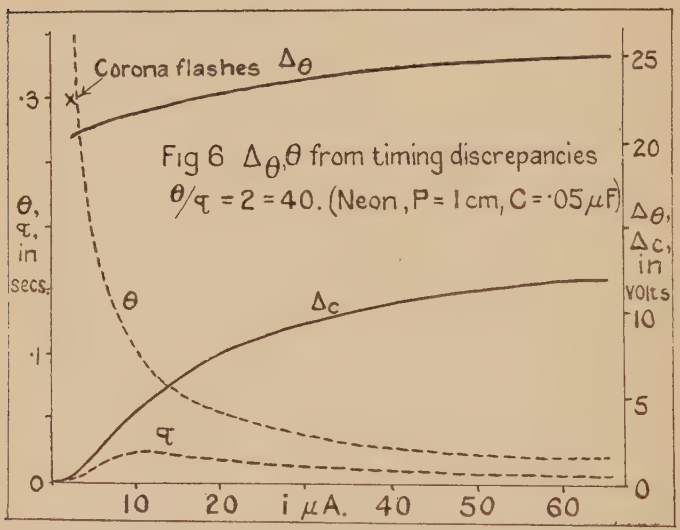


first normal flashes, should show a progressive rise at a diminishing rate. τ is a maximum at the second point of inflexion.

Fig. 6 shows that the agreement with observation, up to $n=10$ or so, is very satisfactory.

The results for various values of C (0·002–1·0 μF.) were equally good. The V_c, i/C curves corresponded not only in form but quite closely numerically, changes of about 20 per cent. only being observed. In Δ_c, $\log i/C$ curves, Δ_c rose very slowly for a small initial stage and then quite quickly at an (almost always) constant rate. Over this range Δ_c equalled $k \log i/C$, k only showing appreciable variation (decrease) when C became quite small. This should follow

Fig. 6.



from the forgoing considerations and from the fact, demonstrated earlier, that the voltage fall during the greater part of build-up is only a volt or two, save in the case of small capacities (< 0·005 F.), where it may approach 10 volts or so ($\Delta_c=40$ volts). Thus for the greater part of τ the voltage-time relation at constant i/C will be essentially the same for most capacities, and Δ_c will be independent of C, with the foregoing exception of the small capacities, where decreases of the order observed are to be expected.

Beyond about $n=10$, conditions are different. Actually, though Δ_c should continue to increase with i, V_c attains a maximum at about $n=20$–40 and then decreases. This is attributable to "overlapping." Examination of V, n curves shows that in most cases this must first occur at about $n=10$.

The total duration of discharge at this stage must thus be of the order of one-tenth of a second. V_C, $\log i/C$ curves show a marked change in Δ_C at this value. This critical n is generally higher for small capacities.

c. θ, τ *Values.*—Sufficiently close values of τ (say 3/4 to 2/3) may be obtained from $\tau = \Delta_C C/i$, and of θ directly by a single-flash method, described previously [4]. Unfortunately this method is not applicable over the full range of values to be treated here. Experimental difficulties preclude the finding of the variation of θ with Δ_M, where the latter is small, as for low frequencies, and the conditions after "overlapping," where Δ_C is largest, are not reproducible with sufficient accuracy. A further difficulty is, that for comparable values of τ and θ to be obtained the voltage variations during build-up should be the same in both cases. Despite this, however, sufficiently reliable results were obtained. They showed that the agreement over the range available was good. Timing relations (later) and single flash experiments confirm this. At overlapping θ was usually some three times greater than τ.

It is at least possible to give the variation of v_m and Δ_C after "overlapping" qualitatively. Single flashes showed that the lag was reduced by the presence of a quite small initial current. Thus on "overlapping," though v would still be approximately equal to v_C until residual currents of 3–4 μA. were present, θ should decrease fairly quickly. v_m would fall as other points on the threshold characteristic were progressively realized, and there would also be rapid decrease of θ. If θ decreased less quickly than i/C increased, Δ_C need not decrease immediately, but could continue to increase for a certain range, though later it must fall, due to the simultaneous lowering of v_m and the reduction of θ. Fig. 5 shows the relations implied. They are in accord with observation.

d. *Clear-up.*—Fig. 1(*a*) shows the effect of a constant charging current superimposed on the V, t relations assumed to hold during clear-up. The voltage will fall rapidly at first (from v_n), reach a minimum value V_B, and then rise at a rate determined chiefly by the value of i/C. After clear-up the V, t curve will be linear; produced backwards it will intersect the time axis ($t=0$) at V_N. The voltage reduction, $v_n - V_N$, must be taken as that equivalent to a quantity transference equal to that actually occurring during clear-up.

The intersection of the charge-up and clear-up voltage curves will be intermediate between V_B and V_N. With

constant clear-up, Δ_B should increase with i/C. Fig. 4 (*a*) shows the form implied.

Fig. 4 (*a*) was obtained in the following way :—Δ_B variations are most easily studied with the V, t relations during clear-up, and hence V_N constant. In intermittence this condition at the best is only approximately realizable, and that only when the points V_C, i corresponding to the various rates of charge lie on the same discharge track (fig. 1, *a*).

In these experiments this condition was satisfied by limiting the driving voltage to a value approximately equal to that of the V_C corresponding to the i employed. These values of V_C were determined empirically (fig. 6, *a*). It is improbable that that v_n, i_n was not approximately constant. The charging current was constant throughout the clear-up period. It was measured at V_B.

In constructing the V, t curve for clear-up (fig. 4, *b*), the "charging" curves were drawn radially from the origin and a point on each midway between V_B and V_N was determined. The results were highly satisfactory. Current-time curves, obtained from these, were of similar form. In the case given the current falls to half value in 0·0005 sec., but the total duration of clear-up is about 0·02 second. The average current is of the order of 1/30 of the initial current.

Similar curves were constructed for different parts of the characteristic by observing the V_C, V_B values for a given condenser charged to definite voltages, and discharged through the tube while known steady currents were flowing. The various values of v_n, i_n could be inferred from the V_C, i values, and clear-up curves drawn as previously. The apparatus defects were too great to permit of more than general confirmation of the results given.

In these experiments V_B was always less than v_b, even when i was many times greater than that for steady conditions. The increased negative glow showed that currents much greater than i could be obtained in flashes. This occurred even with very low values of V_M, though how close to R (fig. 1) has not yet been determined [5]. As suggested, either extinction or radical changes in the characteristic must have occurred in all these cases.

One aspect of fig. 4 (*b*) remains to be discussed. It has been assumed that V_N was not affected by voltage changes during clear-up. Previous considerations show that the quantity transference will be greater and V_N will diminish as i/C, and hence as V_B, is increased. The points plotted should therefore lie on a succession of clear-up curves tending to a decreasing V_N, and with an increasing time duration. Despite this, since

the voltage V_N utilized in the foregoing construction should be the one to which the condenser is tending at the moment V_B is reached, and as the changes up to this moment will not differ greatly in the various cases, the curve given will approximate quite closely to the one required.

Great changes, however, must be produced during the final, small current stage, particularly where n is greater than 6 or 7. Here the final voltage is of the order of v_c, and is many times higher than V_N. This point will be returned to later.

6. V_C, i_n, V_N, V_B Variations.

The i_n, v_n, and hence the V_N variations in intermittence can be deduced from the V_C, i values. The discharge tracks on leaving these points must be considered. Though almost constant at first ($V_C = v_c$), i_n will increase very rapidly as V_C increases. It will then slowly attain a maximum (near maximum V_C). From this stage i_n will show small changes, if any. They will be regular. These inferences are in agreement with observations on the extent of the negative glow.

V_N, i^n clear-up curves (fig. 2, *b*) show that V_N will fall rapidly after a small initial stage of constancy, will slowly pass through a minimum, and then remain constant or rise slowly.

Superimposing on these curves corresponding Δ_B changes (fig. 4, *a*), we find that V_B will be initially (almost) constant, will then fall rapidly, pass through a minimum, and then rise at a steadily diminishing rate.

As fig. 5 shows, these inferences are in complete accord with observations.

As V_N was almost constant, or changed regularly, for a wide range of frequencies ($n > 30$, say), the V_B curve produced backwards to $n=0$ gave V, i/C curves similar to that of fig. 4 (*a*) & (*b*).

The times of clear-up for the large neon-filled tube, $\theta_N = 0{\cdot}015$ sec. for $\Delta_N = 40$–50 volts, utilized earlier, were obtained in this way.

7. Timing Relations.

The time of flash, T, is usually expressed as a function of C, i, and a voltage difference (eqn. 4), say E.

In this paper the variations of E,

$$E = Ti/C, \quad \text{i.e. } \propto i/n,$$

are determined, and it is shown that they may be explained in terms of build-up and clear-up phenomena.

Fig. 1 (*a*) shows that E equals $V_\theta - V_N$, where V_θ is the voltage that would be attained in a time θ after "striking," ($\Delta_\theta = V_\theta - v_m$), and $C(v_n - V_N)$ is the quantity transference actually taking place during clear-up up to the moment of "striking." It will be seen that where "overlapping" occurs the voltage intercept V_N will be higher than that V_N determined from V_B curves, by a voltage equal to that the condenser has yet to fall for complete clear-up. As this is only appreciable for large rates of charge (high n) where the variations of V_N are quite unambiguous, it may be neglected, more especially as the error at a maximum is only about 5 per cent. of $v_n - V_N$.

It has been shown that V_N may easily be determined from V_B, i curves, the error being smallest for low values of the frequency. This permits V_θ ($= V_N + E$) to be found accurately, and the observed variations of Δ_θ and Δ_C, and of θ and τ, to be compared with those required by theory.

a. V_θ *Variations.*—Consistent results for V_C, V_B, n and i relations were obtained in all cases. The variations of E are bound up with those of n with i. From $i=0$ n increased at a gradually increasing rate till a frequency of about 40 was reached. The rate then became constant, the n, i graph between $n=40$–100 (say) being a straight line, which produced to $n=0$ gave an intercept of low value on the i axis. Above $n=100$ the rate of increase of n again changed, increasing progressively with i. E was thus practically constant for an intermediate range, decreasing slowly for low and rapidly for high values of n.

Where V_C was maximum Δ_θ was from 2–6 times greater than Δ_C, but V_θ rapidly approached V_C for higher frequencies; this implies very small lags. No numerical results need be given (fig. 5). The weak subsidiary discharges sometimes occurring between flashes were not observed in these experiments. Their effect would probably have been inappreciable.

Table III. gives results for low values of n, where the Δ_θ and Δ_C variations are most pronounced and definite, and where the values calculated for θ are most capable of verification. They are for the large neon-filled tube, $C = 0{\cdot}05\ \mu F.$, and show the V_C, V_B, V_i, n variations already discussed.

The values obtained for Δ are as described (fig. 6). As previously[4], θ varied somewhat hyperbolically with Δ_C. It had values of 0·6 sec. with V_C near v_c. The ratio of τ/θ increased as i/C was reduced. Values of from 2–50 were recorded.

Results obtained with C=0·005 μF. were of precisely similar form and the Δ_c variations were of the same order, but the corresponding τ/θ ratios were some 2–3 times greater.

TABLE III.

i	3·0	4·3	6·0	9·4	14·7	21·9	35	40	70	
u	·5	·67	·97	1·5	2·35	3·6	5·3	6·05	10·85	
$V_c - V_s$	100	101·7	103·7	106·8	110·3	113·4	116·9	117·7	119·7	
E	120+	121·3	122·5	124·1	126	128	130·7	132	133	
$\Delta\theta$	20·4	20·8	21·2	21·4	22·0	22·8	24·1	24·5	25·5	
θ	·34	·24	·18	·11	·075	·052	·034	·03	·018	
τ	·008	·012	·017	·012	·021	·018	·014	·012	·009	
Δ_c	·5	1·0	2·0	4·0	6·0	8·0	10·0	10·5	12·0	
τ	·0044	·0060	·0081	·0100	·0097	·0061	Upper, C = ·05 μF.			
θ	·36	·24	·16	·10	·072	·038	Lower, C = ·005 μF.			
$\Delta\theta$	41	40·2	40·2	41·9	44·5	49·6	"Overlap," $\Delta_c = 10·5$ $\Delta_c = 7·0$			

This, and the difference in θ, are due to the fact that the values of C where the fall of voltage during the initial stages (τ) of build-up have been reached.

Timing relations were obtained from corona flashes in an analogous manner. Some difficulty is experienced in measuring the currents accurately for this regime, but calculations are simplified by the fact that v_m and V_N closely correspond to v_c (V_C) and V_B respectively. Unfortunately, the actual voltage readings are rather unreliable. In all cases results were in close agreement with those for normal flashes, comparison being possible at the transition current for these two forms. A typical result is indicated in the diagram (fig. 6).

Though these considerations have also been extended to the case where the circuit includes a simple resistance, as in the previous work with which the author was associated, no comment is necessary in the absence of any conflicting evidence whatever.

b. "*Overlapping*" *and* θ_N.—An additional check to the results obtained is possible. The time of flash, T, at the first appearance of overlapping must correspond to the full duration of discharge .and must equal $\theta + \theta_N$. θ is known. Two values

Table IV.

C.	θ.	T.	T$-\theta$.	θ_N^{graph}.	Ratio.
·05	·03	·15	·12	·01 8	7·0
·005	·04	·10	·06	·011	5·5

of θ_N so obtained (large neon-filled tube) are compared, in Table IV., with those determined from V_B, i and clear-up curves. The time for I to fall to 0·01 μA. is taken, this being a reasonable limit to fix for the smallest current by which θ would be appreciably affected in the existing circumstances.

Marked discrepancies are seen to exist, but it will be shown that this is quite consistent with the arguments previously adduced.

The graphical construction employed is accurate for the small current (final) stage of clear-up, only if the voltage is V_N throughout. Actually V must vary between V_N and v_m during this period, being highest at the final stages. Thus it is certain that the clear-up, though not increased appreciably, will be considerably prolonged. The ratios given in the table accord quite well with this explanation. Unfortunately, it is impossible to apply the $\theta_N \propto 1/\Delta_N$ relation here (eqn. 3), since that was obtained only in the case of fully-developed

discharges, and the space-charge in overlapping corresponds to corona currents, for which numerical data are not available.

A further aspect of clear-up phenomena is also involved. The currents (I) in similar V, t graphs will vary as the capacity; "overlapping" depends on I. From the point of view of voltage changes θ_N varies as $1/\Delta_N$, but from the point of view of current it will depend greatly on the size of the capacity. So far as they have been available, "overlapping" results support this. Table IV., where V_N varied from 40–50 volts, gives representative examples. The different time distribution of voltage must also be taken as playing a significant part in this connexion.

Quantitative examination of clear-up currents at overlapping have not yielded data of much significance up to the present, in the absence of any means of checking the results obtained.

c. *Lag Variations.*—The conclusiveness of these observations was apparently shaken by one fact—that, in some cases, especially in the region of the maximum V_C, E calculated was almost of the same value, or even less than $V_C - V_B$.

This fact is quite easy of explanation, if an erratic lag—as, indeed, was generally shown in other ways in such cases (*e. g.* preliminary discharges)[4]—is assumed. Owing to the measuring system employed, the values of V_C and V_B in these cases would be extreme values, whilst the frequency observed would be a mean value. E, and V_C and V_B, would then exhibit the relations recorded. Erratic variation of the frequency, as sometimes is observed, is explainable in a similar manner.

The fact that the lag and the characteristic may change during discharges is demonstrated by the frequently occurring phenomena of normal flashes being preceded by a varying succession of corona discharges. Also, in such tubes, the lag is much smaller after a long period of disuse, and v_e is appreciably lower. When the tube is put into use, v_m and V_C show a regular increase with time until the final, stable, value is attained. The lags, demonstrated by V_C, thus also increase regularly, until finally d finite and repeatable values are recorded. The same effect is demonstrated when a tube is suddenly put into use the frequency only becoming constant after a definite interval of time.

Mention of the effect of light on the lag was made previously. It was demonstrated in a marked manner with

corona flashes, the frequency and the conditions for transition to normal flashes being profoundly modified even by faint illumination. Such phenomena have been the subject of practical application [6].

It will be seen that no definite distinction has been drawn between lag and corona characteristic changes; they are closely, if not indistinguishably, related.

The significance of the lag in the problem of stability is, of course, obvious.

Conclusion.

The foregoing experiments prove that considerable time-lags exist in discharge-tubes when quite appreciable currents, whether due to ionization factors or to the persistence of ionization during the clear-up, are flowing in the "dark period." These lags are at least one hundred times greater than those to be expected from an effect proceeding from the time required to build up a discharge in the gas. Further, the "chance electron" theory would appear to be disproved for these cases. The lags may be traced to a cathode-gas interface effect, which is modified by the action of radiation in such a way as to bring about a diminution of the lag, and either an actual change in the sparking potential, or a virtual change due to the production of a threshold current.

The results in either case are definitely that:

1. Though the sparking potential is lowered, the apparent sparking potential (peak voltage, V_c) will be greater than this statical sparking potential by an amount $\Delta_c = \tau i/C$, where τ is the effective lag and i/C the rate of charge. Thus V_c may correspond to an apparent increase in the sparking potential.

2. If the capacity is small, as for example in most discharge systems at high pressures, the properties of the corona characteristic are such that though discharges may occur they will not be sparks (or normal flashes) unless the lag is greatly reduced by the foregoing or other causes [7]. The occurrence of a spark is really only evidence that the transition stage from one type of discharge to another has been attained.

Finally, the writer would like to record with gratitude his indebtedness to Professor Ornstein for his sustaining interest in his researches and for the facilities so unreservedly placed at his disposal.

Summary.

1. The sequence of phenomena and the variations of the maximum and minimum voltages (V_C and V_B) in the intermittent discharge are studied. The rate of charge is shown to be the significant variable.

2. The theory of the corona lag at "build-up" is discussed. It explains the V_C variations. The additional variations at higher frequencies are due to "overlapping" of discharges. Both the lag (θ) and the "striking" potential (v_m) are lowered.

3. V_B variations under constant clear-up conditions (constant final voltage, V_N) are examined. Current-Voltage-Time relations for clear-up are obtained. The current falls with time in a somewhat exponential manner. Times are of the order of 0·02–0·05 sec.

4. V_B variations in intermittence are shown to depend on the variation of clear-up with V_C and the rate of charge. The time of clear-up (θ_N) is obtained from the graphs.

5. The timing relation, $T=CE/i$, is discussed. E is the difference between V_θ ($=v_m+\theta i/C$) and the virtual V_N.

6. E is everywhere greater than $V_C^e-V_B$. The V_θ variations derived give results in both qualitative and quantitative agreement with prediction.

7. At "overlapping" $T=\theta+\theta_N$. θ_N values so derived differ from those determined graphically. This is shown to be in accord with theory, as are the apparent timing anomalies due to erratic lags.

8. Corona lag variations are briefly discussed.

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CXXII. *A new form of Voltmeter for measuring the Average Voltage for Alternating Currents.* *By* JAMES TAYLOR, *D.Sc., Ph.D., Mackinnon Student of the Royal Society, Trinity College, Cambridge* *.

Introduction.

IN a previous paper (Journ. Scient. Instrs. iii. p. 113, 1925) the writer has considered an application of the diode to the measurement of A.C. voltages.

If a symmetrical alternating potential is applied to a hypothetical resistance R, which is characterized by the property of perfect unilateral conductivity, one-half of the voltage wave-form will be suppressed and an average current $\bar{i}$ (as given by an A.C. instrument in series) will be registered ; namely,

$$\bar{i}=\frac{\int_0^{\tau/2}\phi(t)\,.\,dt}{\tau\,\mathrm{R}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the alternating potential form is given by the relation

$$\mathrm{V}=\phi(t),$$

t being the time-phase and τ the total time-period.

The above ratio of the integral expression to the time-period is, by definition, half the value of the arithmetical average V, so that we may write

$$\bar{i}=\frac{\overline{\mathrm{V}}}{2\mathrm{R}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Such a system as imagined above could be applied to A.C. measurements.

Practical Method.

The above principle may be approximated to by use of a thermionic valve method.

A triode FGP, of which the grid and plate are short-circuited, is connected in series with a resistance R (of suitable magnitude, see later) and a microammeter A. The voltage to be measured is applied across the terminals $\mathrm{T_1}$ $\mathrm{T_2}$. R is adjusted to be about one megohm, if voltages of some 10 to 200 are being measured.

If $\mathrm{T_1}$ $\mathrm{T_2}$ are short-circuited, as a rule a small current is registered because of the pressure of the electrons emitted

* Communicated by Sir J. J. Thomson, O.M., F.R.S.

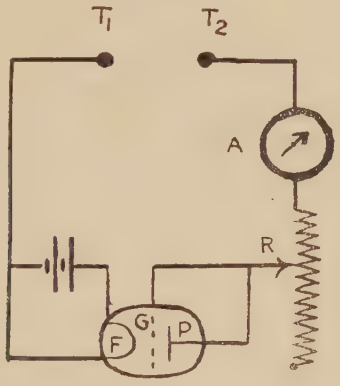
by the filament. This small current may be eliminated by including a small potentiometer in the circuit and adjusting so that no current flows when T_1 T_2 are short-circuited. The error arising from this electron pressure is usually less than a volt.

The instrument may be calibrated on D.C., and then applied to the measurement of average or R.M.S. values of A.C. voltages.

Theory of the Method.

The method depends upon the fact that the voltage taken across the valve is very small relative to that across the resistance R.

Fig. 1.



Assuming a valve volt-ampere characteristic of the form given by Langmuir,

$$i = k \cdot u^{3/2},$$

where u is the voltage across the valve and k is a constant, it was shown that the expression for the current for a D.C. voltage V is given by

$$i = \frac{V}{R}\left[1 - \frac{1}{V^{1/3}(kR)^{2/3}} - \frac{2}{3}\cdot\frac{1}{V^{2/3}(kR)^{4/3}}\right], \quad . \quad . \quad (3)$$

and that for a S.H.A. voltage by (use of Γ-functions)

$$\bar{i} = \frac{\bar{V}}{2R}\left[1 - \frac{1{\cdot}04}{\bar{V}^{1/3}(kR)^{2/3}} - \frac{0{\cdot}73}{V^{2/3}(kR)^{4/3}}\right], \quad . \quad . \quad (4)$$

$\bar{V}$ being the average voltage of the S.H. wave.

Comparison of these equations shows that the ratio is very nearly one-half, since the second and last terms have

coefficients of almost equal value, and, further, the terms are themselves small compared with unity.

It is evident that the law of conductivity for the resistance R is approximately that given in the hypothetical case above.

In the previous work the method was applied only to the measurement of S.H.A. voltages, and it was found extremely satisfactory.

In the case of an arbitrary symmetrical alternating potential expressed by the relation $V = \phi(t)$ (see above), provided the average value,

$$\frac{\int_0^{\tau/2} \phi(t) \, . \, dt}{\tau},$$

is great compared with the maximum value of u the voltage taken by the valve, the instrument gives an accurate half average value of the alternating voltage over the whole period. This condition for accurate performance is equivalent to the statement that the valve constant k must be sufficiently large to maintain a current of the value indicated by the D.C. microammeter at a voltage small compared with those being measured. In a general way this condition is satisfied.

The instrument is useful for the comparative measurement of square voltage wave-forms, such as are given by certain types of commutators supplied by direct voltage, and for those approximately square voltage forms associated with the condenser "flashing" in low potential intermittent discharges, a well-known example of which is the neon lamp intermittent discharge.

There is also the great advantage of an open and regular scale throughout the region. By the use of suitably chosen interchangeable resistances a very large range of possible voltage measurements may be obtained. This method of increasing the range has been utilized recently from voltages of about five volts to several hundreds.

Further, because of the small power consumption it is possible to utilize the voltmeter for the measurement of alternating current (for example, in parallel with a standard resistance).

There is no necessity for frequent calibration; indeed, a new valve may be substituted without the need of making a new calibration. Numerical data in connexion with this point were included in the previous paper which has been referred to.

CXXIII. *Notices respecting New Books.*

Manual of Meteorology. Vol. 1.: *Meteorology in History.* By Sir Napier Shaw, with the assistance of Elaine Austen. Pp. xx+339, with 18 plates. (Cambridge: At the University Press. 1926. Price 30*s.* net.)

THE fourth volume of this work appeared eight years ago, at a time when an account of the subjects dealt with was urgently required for aeronautics. The remaining volumes have been long awaited, and we may express the hope that the remaining two volumes will not now be long delayed.

The purpose underlying the whole work cannot be expressed better than in the author's own words: "The object of the book is to present the study of meteorology, not only as making use of nearly all the sciences and most of the arts, but also as a world study of a special and individual character, going back inevitably to the very dawn of history, and beyond that to the mazes of geological times."

In the present volume the author claims to "have tried to represent the knowledge which the reader of a paper on meteorology before a learned society of the present day will assume, perhaps unconsciously, to be in the possession of his audience." It is not a history of meteorology, but under the guise of the development of meteorological theories and observations through the centuries much valuable information is imparted to the reader, including details of instruments employed for investigations not only of the surface air but also of the upper air; instruments for special purposes are also described, such as pyrheliometers, radiometers, dust-counters, thunderstorm recorders, etc. A chapter is devoted to the development of arithmetical and graphical manipulation.

The earlier chapters are devoted to an account of the meteorology of the world as known to the ancients; to the views of Herodotus, Aristotle, and others on meteorology; to weather-lore and to the question of variability of climate in historical times as far as the Mediterranean region is concerned. The dawn of meteorology as a science is illustrated by short biographies of seventy-four scientific worthies chosen as representing work which has helped to furnish the "instrumental, observational, and intellectual equipment of the exponents of the modern science of meteorology."

The beginnings of international co-operation in the study of meteorology are dealt with in a chapter giving an account of the first meteorological conferences.

The volume is excellently printed. Sir Napier Shaw writes in a stimulating manner, and the volume can be read with interest and pleasure not only by those who are workers in meteorology, but by a far wider circle.

Das Polarisationmikroskop: seine Anwendung in der Kolloid-forschung und in der Färberei. Von H. Ambronn und A. Frey. (*Kolloidforschung in Einzeldarstellungen*, Bd. 5.) Pp. x + 195, with 48 figures and 1 plate. (Leipzig: Akademische Verlagsgesellschaft m. b. H., 1926. Price 13.50 R.M.)

This volume is an elementary book written more especially for those with little mathematical knowledge, to enable them to use the powerful method of colloid investigation which is opened by the polarization microscope, It contains an elementary treatment of polarization and interference phenomena, which gives sufficient details for a working knowledge for the benefit of those to whom these subjects are new. This is followed by an account of various methods of investigation and determination of phase differences, and by practical details connected with the use of the polarization microscope. The second part deals with double refraction phenomena in dispersoid systems, and the third part with various optical methods which lead to information about the structure of such systems.

The polarization microscope is destined to play an increasingly important part in colloid investigation. This little handbook will serve as a useful introduction to the subject for those to whom it is new.

New Methods in Exterior Ballistics. Prof. F. R. Moulton Pp. vi + 258, with 38 figures. (Chicago: University of Chicago Press. London: Cambridge University Press. 1926. Price 20*s*. net.)

This volume contains a brief account of some methods of external ballistics. It arises out of the duties imposed upon the author when he was placed during the war in charge of the Ballistics Branch of the Ordnance Department of the United States Army. He states in the preface that classical ballistic methods were wholly inadequate for current demands and not well suited to the solution of the problems involved. "Accordingly the subject was taken up anew by the author as a scientific problem requiring close co-ordination of adequate theory and well-conducted experiments. In view of the complete independence of the present developments from those that have gone before, no attempt has been made to treat the question historically, nor even to connect these results with those of earlier writers."

This claim is a large one, which does not appear to be fully justified, and the methods used are, in fact, not in general new. The differential equations of motion of a projectile are developed, the resistance function is then considered, and the effect of air resistance is treated by the methods of finite differences. The effects of abnormal air densities, of winds, of the rotation of the

earth, of variations in gravity, of curvature of the earth's surface, &c., are studied by the familiar method of differential variations. The motion of a rotating projectile is discussed by means of Euler's equations, and related problems, such as the oscillations of projectiles, are considered.

The treatment is mathematical throughout, and the volume is not intended for computers. It will be found of value to those interested in ballistics, though it is to be regretted that the work of earlier writers was not considered, and some of the results of recent independent researches included.

The Internal Constitution of the Stars. By A. S. Eddington, M.A., LL.D., D.Sc., F.R.S. Pp. viii + 407, with 5 diagrams. (Cambridge: at the University Press. 1926. Price 25*s.* net.)

Prof. Eddington has performed a valuable service in giving this connected account of the present state of the researches into the physical conditions in the interior of stars. The theory as it stands at present is largely his own work; as the theory has developed, various modifications have had to be made, and in referring to some of the earlier papers it is not infrequently difficult to ascertain exactly what assumptions are being used. The present volume overcomes this difficulty.

Although the theory is not free from serious difficulties, such as the explanation of the phase relationship between the light and velocity variations of Cepheid variables or the source of supply of energy in the interior of a star, it now commands general assent in its broader outlines, and fits in well with observational data. The time is therefore ripe for a connected mathematical account of the theory.

The book is characterized by the author's accustomed lucidity of style. The reader is also impressed by his physical intuition. Many of the mathematical problems to be faced can only be treated with the aid of simplifying assumptions; for these physical intuition is necessary in order to ascertain what approximations may be legitimately employed.

The introductory matter to the theory proper includes a general survey of the problem, and chapters on the thermodynamics of radiation and on the quantum theory. The concluding chapters are outside the main line of investigation, and deal with the outside of a star and with diffuse matter in interstellar space.

The methods and results of the theory have not been free from criticism. The value of the volume would have been enhanced if Prof. Eddington had considered these objections at greater length and the manner in which they may be met. To the onlooker, interested in the theory but taking no part in its development, some of the opposing views have at times proved rather puzzling, and a less cavalier treatment of rival views would have proved welcome.

The Elements of General Zoology. A Guide to the Study of Animal Biology, correlating Functions and Structure, with Notes on Practical Exercises. By WILLIAM J. DAKIN, D.Sc., Professor of Zoology in the University of Liverpool. 8vo. Pp. xvi+496, text-figs. 252. (Oxford University Press. 1927. Price 12*s.* 6*d.*)

PROF. DAKIN has endeavoured to meet the criticism that Zoology is inferior to Botany as a subject for a school curriculum, owing to the difficulties in its experimental treatment. The mere study of structure as apart from function is uninspiring, but Prof. Dakin has shown that function and structure may be treated together, and that experiments are possible with a limited expenditure on apparatus and with material which is readily obtainable.

The subject-matter of the book does not follow the usual systematic arrangement, but is grouped under the headings of the various functions such as nutrition, respiration, blood-circulation, movement, sense, growth, reproduction, and others.

One difficulty has been to give sufficient information on structure to make intelligible the function without unduly increasing the size of the book. This has been done by means of clear annotated drawings and diagrams illustrating the anatomy of various types of animals.

In order to meet the needs of laboratory work where one type at a time will probably be studied throughout, the references in the index have been grouped under special headings; thus under Crayfish will be found references to this animal collected from all parts of the volume.

The book has been admirably produced by the Oxford Press, and is a marvel of cheapness. The illustrations call for special commendation, and the author is to be congratulated on having been able to borrow so many suitable from other works.

The Scientific Work of the late Spencer Pickering, F.R.S. Print for the Royal Society. (Harrison & Sons. 1927. Price 4*s.*)

PROF. A. HARDEN contributes an introductory biographical sketch of this remarkable investigator in widely different branches of Science, in physical chemistry and in the scientific and experimental study of the many problems connected with horticulture.

The first part of the volume, edited by Prof. Lowry, describes the researches in thermochemistry—Pickering's adjustable thermometer anticipating by two years that of Beckmann—theory of solution, colloid chemistry and valency.

The second part, edited by Sir John Russell, deals with Pickering's investigations on the growth of fruit-trees, the method of planting, the effect of grass, and the problems of the pests and diseases of fruit-trees.

His work on the Experimental Farm at Woburn has been described by Sir Daniel Hall "as the most substantial contribution of the last hundred years to the study of fruit-tree development."

Theory of Equations and the Complex Variable. By RAICHARAN BISWAS. (Chuckervertty, Chatterjee & Co., Calcutta.)

PROF. BISWAS has made a successful attempt to set out the Theory of Equations "from the standpoint of complex numbers." After the earlier chapters on the representation of complex numbers, Descartes' Rule, and the Theorems of Rolle and Sturm, the author introduces the "Biradical" transformation to derive the equation of the "squared differences" and the equation of the "semi sums" of the roots of an equation. Some interesting and useful applications to the solution of cubic and higher equations are given.

The approximation of the numerical roots of equations, determinants, and elimination are considered in later chapters.

Attention should be drawn to the numerous helpful exercises, some fully worked out by the author, others with answers only.

High Vacua. By G. W. C. KAYE. (Longmans, Green & Co. 1927. Price 10*s.* 6*d.*)

MANY researches in modern physics have been largely dependent for their success on the efficiency of vacuum pumps, and physicists are indebted to the author for producing a comprehensive, interesting and up-to-date treatise on this subject. Dr. Kaye traces the historical development from the mechanical pump of von Guericke and his "Magdeburg" hemispheres to the most recent high-speed pumps of Gaede and others—rotary mercury, molecular, and mercury-vapour pumps. Details of high-vacuum technique, joints, traps, leaks, cut-offs, "jetters," and backing pumps are set out.

A very complete account is given of the various high-vacuum gauges in use, the earlier instrument of McLeod and its later modifications, the radiometer and leaf-gauges of Knudsen, and other recently introduced gauges depending on gaseous, thermal, and electrical conductivities.

There is some satisfaction in noting that "during the last few years commercial high-vacuum technique of lamps and valves has made great strides" in England.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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Printed by Taylor and Francis, Red Lion Court, Fleet Street.